AZOMETHINE COMPOUNDS

FIG. 1

AZOMETHINE COMPOUNDS

FIG. 1
The present disclosure relates to the polymerization of azomethine and acylhydrazone polymers, and also to the dynamic polymerization of such polymers. The present disclosure further relates to conjugated fluorescent azomethine copolymers. The disclosure also includes azomethine compounds having electrochromic properties, as well as the use of such compounds in electrochromic devices.

When covalent polymers are formed, they have inherent properties that cannot be modified. For example, their degree of polymerization, color, T_g, molecular weight, cannot be changed. Property modification requires substantial postpolymerization chemical modification. Typically this is done at the polymer terminus. However, this is not possible with covalent polymers and their color in addition to other intrinsic opto-electronic properties cannot be modified.

Covalent polymers consisting of azomethines (=N=CH-) or acylhydrazones (-C(0)NRN-) are only sparingly soluble in high boiling point polar solvents such as DMAC and DMF. The said polymers can be made soluble in standard organic solvents such as THF, chloroform, dichloromethane, and acetonitrile by incorporating long solubilising alkyl groups. Instead of incorporating solubilizing groups, azomethine or acylhydrazone polymers can be prepared by coating a substrate with the requisite monomers. Polymerization is then done by heating the substrate in the presence of a catalyst. Pure polymers immobilized on the substrate are obtained after rinsing with a solvent in which the monomers are soluble with a given weight % of base.

Conjugated materials have drawn much attention because of their opto-electronic properties that are suitable for use in plastic electronics including organic photovoltaics, organic field effect transistors, and organic light emitting...
diodes (OLEDs), to name but a few. Polyfluorene derivatives are particularly interesting. This is in part owing to their intrinsic high degree of fluorescence making them ideal for OLED applications. As a result, much effort has been dedicated to preparing new fluorene materials with enhanced properties including high brightness and pure color of emission.

The preparation of polyfluorenes is possible by well-established protocols, including Gilch, Horner-Emmons, Suzuki, Yamamoto, and Stille protocols. While high conversions are possible with these methods, they require stringent reaction conditions. Additionally, pristine polymers with high color purity are obtained only after substantial product purification.

Polyazomethines are interesting alternatives to conventional coupling protocols. This is in part owing to their straightforward preparation that does not require stringent reaction conditions or co-reagents. Water is also the unique reaction by-product. Therefore, extensive purification for removing side products and co-reagents is not required. In fact, pristine polymers are obtained upon solvent evaporation or by simple precipitation.

While azomethines are isoelectronic to their vinyl analogues and their preparation is synthetically advantageous relative to their carbon counterparts, they have not been pursued as functional materials for use in plastic electronics. This is partly because they are understood to be both hydrolytically and oxidatively unstable. More importantly, all previously investigated conjugated polyazomethines were non-fluorescent, despite incorporating intrinsically fluorescent monomers.\textsuperscript{1,2} Accurate opto-electronic property evaluation was further problematic because of the limited solubility of previously reported polyazomethines in common organic solvents.

The optical property limitations and solubility issues encountered with previously investigated polyazomethines was recently addressed.\textsuperscript{3,4} This was in part owing to the use of C10 groups. This led to highly soluble
polyazomethines whose molecular weight could accurately be measured using standard methods. While hydrolytically and oxidatively robust polyazomethines were possible,\(^3\) they were not fluorescent. The first example of a fluorescent homo-polyazomethine (PFI-co-FI) was however possible by using the 9,9-dihexyl-2,7-diaminofluorene monomer \(^1\).\(^5\) In fact, the absolute \(\Phi_i\) (0.4 in thin films) of the all-fluorene polyazomethine was comparable to polyfluorene prepared by common aryl coupling protocols.\(^6\)

[0009] Functional materials with electrochemically switchable colors between their neutral and radical ion \((on/off)\) states and capable of displaying a large palette of colors are required to meet the demands of consumer and commercial electronics. Materials capable of such color switching have found uses in stealth technologies, camouflage materials, textiles, curtainless windows, pricing display signs, transparent refrigerator doors, sun roofs, electronic displays \((e.g.\ i-phone)\), sunglasses, and telecommunications switches.\(^7\) Recently, electroactive materials have been successfully used in electronic-paper and electronic-readers along with smart-cards, which display real-time balances on various cards including transportation, parking, and personal credit.

[0010] The preparation of electrochemically induced color-switchable compounds however requires rigorous reaction conditions such as anhydrous solvents, inert atmospheres, and catalysts.\(^8\)\(^9\) These coupling methods also produce significant by-products, requiring product purification in order not to compromise the materials' color and performance. These not only make materials preparation challenging, but they also make their fabrication expensive. The prepared polymers must also be soluble in solvents compatible with either spin- or spray-coating methods. Making the polymer soluble for use in coatings also makes them miscible in standard electrolyte gels, potentially leading to localized short-circuits. The collective problematic effects make the device in which these materials are to be incorporated expensive and challenging to produce. Meanwhile, localized short-circuiting limits the device longevity and
dilutes the color transitions between the on/off states. Moreover, the materials used for color switching in ECDs suffer from a limited color palette and are a mere two-color state. Alternate straightforward coupling methods not requiring stringent protocols and simple- to no-product purification are therefore desired for preparing new electrochromic functional materials that are both cost-effective with a large range of tuneable colors.

[0011] New functional organic materials consisting of azomethines linkages (-N=CH-) have been disclosed. Not only are these compounds much easier to prepare than their conventional counterparts, but also water is the only by-product produced. They are further environmentally-friendly and cost-effective and require minimal purification. In addition, the colors of these compounds can easily be tuned contingent on easily prepared or commercially available starting materials.

[0012] Despite their synthetic and ecologically advantages, azomethines have not been pursued as electrochromic materials (EM) for use in electrochromic devices (ECDs). This is a result of previously investigated homoaryl azomethines that were irreversible oxidized combined with possessing high oxidation potentials (> 1.2 V). Azomethines are further understood to be hydrolytically unstable and readily decompose, resulting in extremely poor device lifetimes. The shortcomings of previously investigated azomethines was addressed by preparing heterocyclic azomethines derived from diaminothiophenes. Not only can the oxidation potential be tailored as a function of structure, but also reversible oxidization is possible, especially when incorporating 2-aminothiophenes into the terminal positions. The colors of their neutral and oxidized states could further be tailored and high contrast ratios between the on/off states were possible. Similarly, the turn-on voltage that induces color changes, can also be adjusted by incorporating electron donating or withdrawn groups in either the central aryl units or terminal groups.
Heterocyclic azomethines are further advantageous because both the neutral and oxidized forms are air stable.

[0013] Conjugated azomethines consisting uniquely of thiophenes are suitable as electrochromic materials in ECDs. Despite possessing key properties for ECD usage, including chemical robustness, reversible oxidization, resistant to repeated oxidation/neutralization cycles, large contrast ratios, and reversible color formation, most heterocyclic azomethines and their derivatives are soluble in common organic solvents. This is problematic because they dewet from the electrode when the electrolyte gel is deposited on top by either spray- or spin-coating. The electrolyte gel is required for both efficient charge transport between the two electrodes and ion storage. Miscibility of the electrolyte gel and EC material results in inconsistent color, variable film thickness of the EC material, color bleaching, limited device performance, and poor mechanical properties. It is advantageous that the EC and electrolyte gel layers do not mix.

SUMMARY

[0014] This disclosure relates to polymers of the formula I

\[
\begin{array}{c}
\text{H}_2\text{N} \left( \begin{array}{c}
\text{N} \left( \begin{array}{c}
\text{R}_1 \left( \begin{array}{c}
\text{N} \left( \begin{array}{c}
\text{R}_2 \left( \begin{array}{c}
\text{R}_3 \end{array} \right) \end{array} \right) \end{array} \right) \end{array} \right) \end{array} \right) \text{O} \\
\end{array}
\]

(I)

wherein,

R1 is alkylene, cycloalkylene, alkenylene, alkynylene, arylene, heteroarylene, NH-alkyl, NH-aryl, N(alkyl)alkyl, N(alkyl)-aryl, or NR4C(0)-R5-C(0)NR4;

R2 is alkylene, arylene or heteroarylene;

R3 is hydrogen, alkyl, aryl or heteroaryl;

R4 is alkyl, aryl or heteroaryl;

R5 is alkylene, arylene or heteroarylene; and
n is an integer from 2 to 100,
wherein the alkyl(ene), cycloalkyl(ene), alkenyl(ene), alkynyl(ene), aryl(ene) or heteroaryl(ene) groups are each optionally substituted with one to five substituents independently selected from halo, hydroxy, CN, C(0)NH2, C\textsubscript{1-14}-alkyl, C\textsubscript{3}-C\textsubscript{10}-cycloalkyl, C(0)-aryl and -C(0)OR, or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, wherein R is H, C\textsubscript{1-6}-alkyl (such as t-butyl) or aryl.

[0015] In another embodiment, the disclosure relates to polymers of the formula II

![Chemical Structure](image)

wherein

- R\textsubscript{6} is as defined for R\textsubscript{1} above,
- R\textsubscript{7} is as defined for R\textsubscript{3} above; and
- p is an integer from 2 to 100.

[0016] In another embodiment, polymers of the formula I and II are capable of undergoing constitutional component exchange, or dynamic polymerization, in which the monomer units which comprise the polymers of the formula I and II are exchanged with compounds of the formula (III), (IV) and (V)

(a) formula (III)

![Chemical Structure](image)

wherein,
\[ R_s \] is as defined for \( R_2 \) above;
\[ R_9 \] is as defined for \( R_3 \) above; and
(b) formula (IV)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{NH}_2 \\
\quad & \quad R_{10}
\end{align*}
\]  
\text{(IV)}

wherein,
\[ R_{10} \] is as defined for \( R_1 \) above;
(c) formula (V)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{O} \\
\quad & \quad R_{11} \\
\quad & \quad R_{12}
\end{align*}
\]  
\text{(V)}

wherein,
\[ R_{11} \] is as defined for \( R_1 \) above;
\[ R_{12} \] is as defined for \( R_3 \) above.

[0017] The disclosure also includes compounds of the formula (Ia)

\[
\begin{align*}
\text{H}_2\text{N} \quad & \quad \left( \begin{array}{c}
\text{R}_{1a} \\
\text{N} \\
\text{R}_{2a} \\
\text{R}_{3a} \\
\text{R}_r \\
\text{R}_{3a}
\end{array} \right) \quad & \quad \text{O}
\end{align*}
\]  
\text{(Ia)}

wherein,
\[ R_{1a} \] is arylene or heteroarylene;
\[ R_{2a} \] is arylene or heteroarylene;
\[ R_{3a} \] is hydrogen or alkyl; and
\[ r \] is an integer from 2 to 100;

wherein the alkyl(ene), aryl(ene) or heteroaryl(ene) groups are each optionally substituted with one to five substituents independently selected
from halo, hydroxy, CN, C(0)NH\textsubscript{2}, Ci\textsubscript{1-4}-alkyl, C\textsubscript{3}-C\textsubscript{10}-cycloalkyl, C(0)-aryl and -C(0)OR, or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, wherein R is H, C\textsubscript{i-C\textsubscript{6}}-alkyl (such as t-butyl) or aryl.

[0018] Compounds of the formula (I), (la) and (II) are conjugated fluorescent azomethine polymers or copolymers. The present disclosure further relates to the opto-electronic, halochromic, and doping properties of these conjugated fluorescent azomethine polymers or copolymers of the formula (I), (la) and (II). In an aspect, given the importance of tuning the emission color for a given emitting application while preserving high $\Phi_e$, the present disclosure relates to polyazomethines and/or copolyazomethines consisting of or consisting essentially of thiophene and fluorene derivatives.

[0019] In an embodiment, the present disclosure relates to the halochromism, chemical oxidation, and electrochromism of the conjugated polyazomethines and/or copolyazomethines of the formula (I), (la) and (II). In an aspect, these properties were explored for demonstrating their resistance towards acid hydrolysis and oxidation.

[0020] In an embodiment, the present disclosure relates to the use of fluorescent conjugated polyazomethines and/or copolyazomethines of the formula (I), (la) and (II) in various electronic devices. In an aspect, non-limiting examples of electronic devices comprise organic electronic devices, including emitting devices as well as sensors.

[0021] The present disclosure further relates to azomethine compounds having electrochromic properties. In one embodiment, the present disclosure relates to an azomethine compound of Formula (VI):
Structure of formula (VI)

wherein:
(a) $R_{i3}$ is selected from the group consisting of CN, C(0)aryl, C(0)NH$_2$ and CO$_2$R$_{18}$;
(b) $R_{i4}$ is selected from the group consisting of alkylene, ortho-arylene, meta-arylene, para-arylene, 1-alkylarylene, alkyl ether, and aryl ether;
(c) $R_{15}$ is selected from the group consisting of H, alkyl, aryl, =CH and =C-alkyl, with the proviso that when $R_{15}$ is =CH or =C-alkyl, the moiety -NH-$R_{15}$ is -N=$R_{15}$;
(d) $R_{16}$ is selected from the group consisting of S, SO$_2$, O, NH, N-alkyl, N-aryl, N-SO$_2$H, N-SO$_2$-alkyl and N-SO$_2$-aryl;
(e) $R_{17}$ is selected from the group consisting of alkyl, O-alkyl, O-aryl, aryl, S-alkyl, S-aryl, NO$_2$, CN, and CO$_2$R$_n$; and
(f) $R_{i8}$ is selected from the group consisting of H, alkyl, and monovalent organic or inorganic cations.

In another embodiment, the present disclosure relates to an azomethine of Formula (VII):

Structure of formula (VII)

wherein:
(a) \( R_{19} \) is selected from the group consisting of CN, C(0)aryl, C(0)NH\(_2\) and CO\(_2\)R\(_{22}\);
(b) \( R_{20} \) is an arylene or heteroarylene;
(c) \( R_{21} \) is selected from the group consisting of H, alkyl, aryl, =CH-alkyl, =CH-aryl, =C-alkyl, 1,4-benzyl-C0\(_2\)-tert-butyl, 1,3-benzyl-C0\(_2\)-tert-butyl, 1,2-benzyl-C0\(_2\)-fert-butyl, =CH-para-phenyl-C0\(_2\)-tert-butyl, =CH-or\( \text{meta} \)-phenyl-C0\(_2\)-tert-butyl, and =CH-meta-phenyl-C0\(_2\)-tert-butyl, with the proviso that when \( R_{21} \) is =CH-alkyl, =CH-aryl or =C-alkyl, the moiety -NH-R\(_{21}\) is -N=R\(_{21}\); and
(d) \( R_{22} \) is selected from the group consisting of H, alkyl, tert-butyl and monovalent organic or inorganic cations.

[0023] In an embodiment, the present disclosure relates to a polymer of the formula (I) which is a polymer of the Formula (VIII):

\[
\begin{align*}
\text{Structure of formula (VIII)}
\end{align*}
\]

wherein:

(a) \( R_{23} \) is selected from the group consisting of CN, C(0)NH\(_2\), C(0)-aryl and CO\(_2\)R\(_{25}\);
(b) \( R_{24} \) is arylene;
(c) \( R_{25} \) is selected from the group consisting of tert-butyl, H, alkyl and aryl; and
(d) \( m \) is from 2 to 50.

[0024] In an embodiment, the present disclosure relates to a method for the immobilization of an azomethine of Formula (VI) on substrates comprising
exposure of an azomethine of Formula (VI) to vapors of an organic, mineral, or Lewis acid catalyst. In a further embodiment, the organic, mineral, or Lewis acid catalyst are selected from the group consisting of trifluoroacetic acid, methane sulfonic acid, triflic acid, hydrochloric acid, sulphuric acid, nitric acid, BF$_3$-etherate, and BBr$_3$.

[0025] In an embodiment, the present disclosure relates to a method for the immobilization of an azomethine of Formula (VI) on substrates comprising irradiating the azomethine of Formula (VI) with electromagnetic radiation with a wavelength of about 254 to about 500 nm wherein the azomethine of Formula (VI) is co-deposited with a photoacid generator in 0.5 to 25 weight %.

[0026] In an embodiment, the present disclosure relates to a method for the immobilization of an azomethine of Formula (VII) on substrates comprising exposing the azomethine of Formula (VII) to vapors of an organic, mineral, or Lewis acid catalyst.

[0027] In an embodiment, the present disclosure relates to a method for the immobilization of an azomethine of Formula (VII) on substrates comprising irradiating the azomethine of Formula (VII) with electromagnetic radiation with a wavelength between 254 to 500 nm wherein the azomethine is co-deposited with a photoacid generator in 0.5 to 25 weight %.

[0028] In an embodiment, the present disclosure relates to a method for the preparation of an immobilized electrochromic material of Formula (VIII) comprising heating a substrate coated with the corresponding monomer(s) of the compound of the Formula (VIII) in the absence or presence of a catalyst.

[0029] In an embodiment, the present disclosure relates to an electrochromic device comprising: a transparent electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VI) on substrates by exposure to vapors of an organic, mineral, or Lewis acid catalyst; a conducting gel; and a counter electrode.
[0030] In an embodiment, the present disclosure relates to an electrochromic device comprising: a transparent electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VI) on substrates by irradiating with a wavelength of about 254 to about 500 nm when the azomethine of Formula (VI) is co-deposited with a photoacid generator in 0.5 to 25 weight %; a conducting gel; and a counter electrode.

[0031] In an embodiment, the present disclosure relates to an electrochromic device comprising: a transparent electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VII) on substrates by exposure to vapors of an organic, mineral, or Lewis acid catalyst; a conducting gel; and a counter electrode.

[0032] In an embodiment, the present disclosure relates to an electrochromic device comprising: a transparent electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VII) on substrates by irradiating with a wavelength of about 254 to about 500 nm when the azomethine of Formula (VII) is co-deposited with a photoacid generator in 0.5 to 25 weight %; a conducting gel; and a counter electrode.

[0033] In an embodiment, the present disclosure relates to an electrochromic device comprising: a transparent electrode; an electrochromic layer prepared via the immobilization of an electrochromic material of Formula (VIII) by heating the substrate coated with the corresponding monomer(s) in the absence or presence of a catalyst; a conducting gel; and a counter electrode.

[0034] In an embodiment, the present disclosure relates to an electrochromic device comprising: a reflective electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VI) on substrates by exposure to vapors of an organic, mineral, or Lewis acid catalyst; a conducting gel; and a counter electrode.
In an embodiment, the present disclosure relates to an electrochromic device comprising: a reflective electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VI) on substrates by irradiating with a wavelength of about 254 to about 500 nm when the azomethine of Formula (VI) is co-deposited with a photoacid generator in 0.5 to 25 weight %; a conducting gel; and a counter electrode.

In an embodiment, the present disclosure relates to an electrochromic device comprising: a reflective electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VII) on substrates by exposure to vapors of an organic, mineral, or Lewis acid catalyst; a conducting gel; and a counter electrode.

In an embodiment, the present disclosure relates to an electrochromic device comprising: a reflective electrode; an electrochromic layer prepared via the immobilization of an azomethine of Formula (VII) on substrates by irradiating with a wavelength of about 254 to about 500 nm when the azomethine of Formula (VII) is co-deposited with a photoacid generator in 0.5 to 25 weight %; a conducting gel; and a counter electrode.

In an embodiment, the present disclosure relates to an electrochromic device comprising: a reflective electrode; an electrochromic layer prepared via the immobilization of an electrochromic material of Formula (VIII) by heating the substrate coated with the corresponding monomer(s) in the absence or presence of a catalyst; a conducting gel; and a counter electrode.

The azomethine/gel layer miscibility and dewetting challenges can be addressed by immobilizing the azomethines on the electrode by making them insoluble in organic solvents. Such a change in solubility can be achieved by cross-linking the azomethines, by converting its ester into a carboxylate, or by incorporating a group that can be thermally removed. Insoluble electrochromic azomethines can also be obtained by depositing pre-polymer materials onto the
desired substrate and then thermally activating their immobilization in the presence of a catalyst.

[0040] The foregoing and other objects, advantages and features of the present specification will become more apparent upon reading of the following non-restrictive description of illustrative embodiments thereof, given by way of example only with reference to the accompanying drawings/figures

[0041] Further aspects and advantages of the embodiments described herein will appear from the following description taken together with the accompanying drawings.

10 BRIEF DESCRIPTION OF THE DRAWINGS

[0042] For a better understanding of the embodiments described herein and to show more clearly how they may be carried into effect, reference will now be made, by way of example only, to the accompanying drawings which show at least one exemplary embodiment, and in which:

[0043] **FIG. 1** is a schematic representation of the polymerization of an AA-BB type polymer, and subsequent component exchange with AA' and BB' monomers;

[0044] **FIG. 2** is a schematic representation of the polymerization of an AB type polymer, and subsequent component exchange with an AB' monomer;

[0045] **FIG. 3** is an illustration of the TGA of various polyfluorenylazomethines: **PFI-co-Th (●)**, **PFI-co-DAT (A)** and **PFI-co-EDOT (·)** at a scan rate of 10 °C/min under N₂. Inset: differential scanning thermograms of PFI-co-Th (●), PFI-co-DAT (A) and PFI-co-EDOT (·) at a scan rate of 5 °C/min under N₂, in accordance with an embodiment of the present disclosure;

[0046] **FIG. 4** is an illustration of the normalized absorbance (A) and fluorescence (B) spectra in solution (filled symbols) and thin film (open symbols)
of PFI-co-Th (■), PFI-co-DAT (·) and PFI-co-EDOT (A), in accordance with an embodiment of the present disclosure;

[0047] FIG. 5 is a photographic illustration of PFI-co-Th (A), PFI-co-DAT (B), and PFI-co-EDOT (C) in dichloromethane under ambient light and PFI-co-Th (D), PFI-co-DAT (E), and PFI-co-EDOT (F) irradiated with a UV lamp at 350 nm, in accordance with an embodiment of the present disclosure;

[0048] FIG. 6 is an illustration of cyclic voltammograms of PFI-co-Th (A), PFI-co-DAT (·), PFI-co-EDOT (■), Th-Fi-Thi (□), and Th-Fi-Th₂ (○) in dichloromethane at a scan rate of 50 mV/s under N₂. Inset: photographs of original (left) and electrochemically oxidized (right) PFI-co-DAT by applying a potential of 1.0 V for 1 minute, in accordance with an embodiment of the present disclosure;

[0049] FIG. 7 is an illustration of the cathodic cyclic voltammograms of PFI-co-Th (■), PFI-co-DAT (·) and PFI-co-EDOT (A) in dichloromethane at a scan rate of 50 mV/s under N₂, in accordance with an embodiment of the present disclosure;

[0050] FIG. 8 is an illustration of the normalized absorbance spectra of PFI-co-EDOT in dichloromethane (A) with the addition of 1 equivalent of TFA (♦), followed by the addition of 1 equivalent of triethylamine (·), a pristine sample of PFI-co-EDOT (A) with the addition of 1 equivalent of FeCl₃ (■), followed by the addition of 1 equivalent of hydrazine hydrate (□). Inset: absorbance of PFI-co-Th monitored at 595 nm as a function of FeCl₃ mole fraction, in accordance with an embodiment of the present disclosure;

[0051] FIG. 9 is a photographic illustration of PFI-co-Th (A), PFI-co-EDOT (B), and PFI-co-DAT (C) in dichloromethane (left), after the addition of FeCl₃ (right), followed by the addition of hydrazine hydrate (right), in accordance with an embodiment of the present disclosure;
FIG. 10 is a GPC chromatogram of PFI-TH (A), PFI-EDOT (♦) and PFI-DAT (*) in THF, in accordance with an embodiment of the present disclosure;

FIG. 11 is an illustration of the normalized absorbance (filled symbols) and fluorescence (empty symbols) spectra of Th-Fi-Thi (●) and Th-Fi-Th2 (○), in accordance with an embodiment of the present disclosure;

FIG. 12 is an illustration of the spectroelectrochemistry of polyfluorenylazomethine PFI-co-DAT at different potentials in accordance with an embodiment of the present disclosure;

FIG. 13 is an illustration of the spectroelectrochemistry of polyfluorenylazomethine PFI-co-EDOT at different potentials in accordance with an embodiment of the present disclosure (Inset: picture of color change on 1.8 V potential);

FIG. 14 is an illustration of the spectroelectrochemistry of polyfluorenylazomethine PFI-co-TH at different potentials in accordance with an embodiment of the present disclosure (Inset: picture of color change at 1.6 V);

FIG. 15 is an illustration of the spectroelectrochemistry of Th-Fi-Thi in dichloromethane in accordance with an embodiment of the present disclosure;

FIG. 16 is an illustration of the Job plot of PFI-co-DAT with FeCl₃ in accordance with an embodiment of the present disclosure;

FIG. 17 is an illustration of the Job plot of PFI-co-EDOT with FeCl₃ in accordance with an embodiment of the present disclosure;

FIG. 18 is an illustration of the oxidation/neutralization of polyfluorenylazomethines: (a) PFI-co-TH, (b) PFI-co-DAT and (c) PF-co-EDOT; original solution (A), presence of FeCl₃ (♦), and presence of hydrazine (★), in accordance with an embodiment of the present disclosure;
FIG. 19 is an illustration of the protonation/neutralization of polyfluorenylazomethines: (a) PFI-co-TH, (b) PFI-co-DAT, and (c) PFI-co-EDOT: original solution (A), with TFA added (♦), and subsequent addition of triethylamine (*), in accordance with an embodiment of the present disclosure;

FIG. 20 is an illustration of the oxidation/neutralization of fluorenylazomethine trimers: (a) Th-Fi-Th-i and (b) Th-Fi-Th₂: original solution (▲), with the addition of FeCl₃ (♦), and subsequent addition of hydrazine (*), in accordance with an embodiment of the present disclosure;

FIG. 21 is an illustration of the protonation/neutralization of polyfluorenylazomethines: (a) Th-Fi-Thi and (b) Th-Fi-Th₂: original solution (A), with the addition of TFA (♦), and subsequent addition of triethylamine (*), in accordance with an embodiment of the present disclosure; and

FIG. 22 is a photographic illustration of the fluorescence of alternating co-polyazomethines consisting of fluorene and thiophene derivatives, in accordance with an embodiment of the present disclosure.

DETAILED DESCRIPTION

(I) DEFINITIONS

In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this specification pertains.

The word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one", but it is also consistent with the meaning of "one or more", "at least one", and "one or more than one". Similarly, the word "another" may mean at least a second or more.
As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "include" and "includes") or "containing" (and any form of containing, such as "contain" and "contains"), are inclusive or open-ended and do not exclude additional, unrecited elements or process steps.

As used in this specification and claim(s), the word "consisting" and its derivatives, are intended to be close ended terms that specify the presence of stated features, elements, components, groups, integers, and/or steps, and also exclude the presence of other unstated features, elements, components, groups, integers and/or steps.

As used in this specification and claim(s), the term "consisting essentially of" and its derivatives, are intended to be close ended terms that specify the presence of stated features, elements, components, groups, integers, and/or steps, and is open to unlisted features that do not materially affect the basic properties of the invention.

The terms "about", "substantially" and "approximately" as used herein mean a reasonable amount of deviation of the modified term such that the end result is not significantly changed. These terms of degree should be construed as including a deviation of at least ±1% of the modified term if this deviation would not negate the meaning of the word it modifies.

The present description refers to a number of chemical terms and abbreviations used by those skilled in the art. Nevertheless, definitions of selected terms are provided for clarity and consistency.

Abbreviations: NMR: Nuclear Magnetic Resonance; MS: Mass Spectrometry; m.p.: melting point; HRMS: High Resolution Mass Spectrometry; SEC: Size-Exclusion Chromatography; $M_n$: Number Average Molecular Weight; PDI: PolyDispersity Index; DP: Degree of Polymerization; DSC: Differential
Scanning Calorimetry; XRD: X-Ray Diffraction (powder diffraction); PDI: PolyDispersity Index; EtOAc: Ethyl Acetate; CH$_2$Cl$_2$: Dichloromethane; CDCl$_3$: Chloroform-d; DMAP: 4-(N,N-dimethylamino)pyridine; TFA: Trifluoroacetic acid; TCDI: 1,1-thiocarbonyldiimidazole; AcOH: Acetic acid; TLC: Thin Layer Chromatography; FAB: Fast Atom Bombardment; FCC: Flash Column Chromatography.

[0073] The suffix "ene" added on to any of the groups herein means that the group is divalent, i.e. inserted between two other groups. When an R group (for example R-1) in a structure has two attachments to other groups, the R group is assumed to be bivalent. For example, alkyl becomes alkenylene; cycloalkyl becomes cycloalkylene; alkenyl becomes alkenylene; alkynyl becomes alkynylene; aryl becomes arylene; heteroaryl becomes heteroarylene etc.

[0074] As used herein, the term "alkyl" embraces straight-chain or branched. Substituted alkyl residues can be substituted in any suitable position. Unless otherwise indicated, examples of alkyl residues include groups containing from 1 to 18 carbon atoms are methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, nonyl, decyl, undecyl, dodecyl, tetradecyl, hexadecyl and octadecyl, the n-isomers of all these residues, isopropyl, isobutyl, isopentyl, neopentyl, isoheptyl, isodecyl, 3-methylpentyl, 2,3,4-trimethylhexyl, sec-butyl, tert-butyl, or tert-pentyl.

A specific group of alkyl residues is formed by the residues methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, sec-butyl and tert-butyl.

[0075] As used herein, the term "lower alkyl" embraces straight-chain or branched. Substituted alkyl residues can be substituted in any suitable position. Unless otherwise indicated, examples of lower alkyl residues include groups containing from 1 to 6 carbon atoms are methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl, pentyl, isopentyl, neopentyl, and hexyl.

[0076] As used herein, the term "alkylene" embraces a linear saturated divalent hydrocarbon radical of 1 to 18 carbon atoms or a branched saturated...
divalent hydrocarbon radical of 3 to six 18 atoms. Unless otherwise indicated, examples of alkylene residues are methylene, ethylene, 2,2-dimethylethylene, propylene, 2-methylpropylene, butylene, and pentylene.

[0077] As used herein the term "alkenyl" embraces straight-chain or branched unsaturated alkyl residues that contain one or more, for example one, two or three double bonds which can be in any suitable position. Of course, an unsaturated alkyl residue has to contain at least two carbon atoms. Examples of unsaturated alkyl residues are alkenyl residues such as vinyl, 1-propenyl, allyl, butenyl or 3-methyl-2-butenyl.

[0078] As used herein the term "alkynyl" embraces straight-chain or branched unsaturated alkyl residues that contain one or more, for example one, two or three, triple bonds which can be in any suitable position. Of course, an unsaturated alkyl residue has to contain at least two carbon atoms. Examples of unsaturated alkyl residues are alkynyl residues such as ethynyl, 1-propynyl or propargyl.

[0079] As used herein the term "cycloalkyl" embraces monocyclic or polycyclic, for example monocyclic, bicyclic or tricyclic, i.e., they can for example be monocycloalkyl residues, bicycloalkyl residues and tricycloalkyl residues, provided they have a suitable number of carbon atoms and the parent hydrocarbon systems are stable. A bicyclic or tricyclic cycloalkyl residue has to contain at least 4 carbon atoms. In an embodiment, a bicyclic or tricyclic cycloalkyl residue contains at least 5 carbon atoms. In a further embodiment, a bicyclic or tricyclic cycloalkyl residue contains at least 6 carbon atoms and up to the number of carbon atoms specified in the respective definition. Cycloalkyl residues can be saturated or contain one or more double bonds within the ring system. In particular they can be saturated or contain one double bond within the ring system. In unsaturated cycloalkyl residues the double bonds can be present in any suitable positions. Monocycloalkyl residues are, for example, cyclopropyl, cyclobutyl, cyclopentyl, cyclopentenyl, cyclohexyl, cyclohexenyl, cycloheptyl,
cycloheptenyl, cyclooctyl, cyclononyl, cyclodecyl, cycloundecyl, cyclododecyl or cyclotetradecyl, which can also be substituted, for example by C1-C4 alkyl. Examples of substituted cycloalkyl residues are 4-methylcyclohexyl and 2,3-dimethylcyclopentyl. Examples of parent structures of bicyclic ring systems are norbornane, bicyclo[2.2.1]heptane, bicyclo[2.2.2]octane and bicyclo[3.2.1]octane.

[0080] As used herein, the term "aryl" embraces an aromatic substituent which is a single ring or multiple rings fused together. When formed of multiple rings, at least one of the constituent rings is aromatic. In an embodiment, aryl substituents include phenyl, naphthyl and fluorene groups.

[0081] The term "halo" means halogens such as fluorine, chlorine, bromine or iodine.

[0082] The term "heterocyclo" as used herein embraces saturated, partially unsaturated and unsaturated heteroatom-containing ring-shaped radicals, where the heteroatoms may be selected from nitrogen, sulfur and oxygen. Examples of saturated heterocyclo radicals include saturated 3 to 6-membered heteromonocyclic groups containing 1 to 4 nitrogen atoms (e.g. pyrrolidinyl, imidazolidinyl, piperidino, piperazinyl, etc.); saturated 3 to 6-membered heteromonocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms (e.g. morpholinyl, etc.); saturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulfur atoms and 1 to 3 nitrogen atoms (e.g., thiazolidinyl, etc.). Examples of partially unsaturated heterocyclo radicals include dihydrothiophene, dihydropyran, dihydrofuran and dihydrothiazole.

[0083] The term "heteroaryl" as used herein embraces aromatic ring containing heterocyclo radicals. Examples of unsaturated heterocyclo radicals, also termed "heteroaryl" radicals include unsaturated 3 to 6 membered heteromonocyclic group containing 1 to 4 nitrogen atoms, for example, pyrrolyl, pyrrolinyl, imidazolyl, pyrazolyl, pyridyl, pyrimidyl, pyrazinyl, pyridazinyl, triazolyl (e.g., 4H-1,2,4-triazolyl, 1H-1,2,3-triazolyl, 2H-1,2,3-triazolyl, etc.) tetrazolyl (e.g.
1H-tetrazolyl, 2H-tetrazolyl, etc.), etc.; unsaturated condensed heterocyclo group containing 1 to 5 nitrogen atoms, for example, indolyl, isoindolyl, indolizyl, benzimidazolyl, quinolyl, isoquinolyl, indazolyl, benzo triazolyl, tetrazolopyridazinyl (e.g., tetrazolo[1,5-b]pyridazinyl, etc.), etc.; unsaturated 3 to 6-membered heteromonocyclic group containing an oxygen atom, for example, pyranyl, furyl, etc.; unsaturated 3 to 6-membered heteromonocyclic group containing a sulfur atom, for example, thienyl, etc.; unsaturated 3- to 6-membered heteromonocyclic group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms, for example, oxazolyl, isoxazolyl, oxadiazolyl (e.g., 1,2,4-oxadiazolyl, 1,3,4-oxadiazolyl, 1,2,5-oxadiazolyl, etc.) etc.; unsaturated condensed heterocyclo group containing 1 to 2 oxygen atoms and 1 to 3 nitrogen atoms (e.g. benzoxazolyl, benzoxadiazolyl, etc.); unsaturated 3 to 6-membered heteromonocyclic group containing 1 to 2 sulfur atoms and 1 to 3 nitrogen atoms, for example, thiazolyl, thia diazolyl (e.g., 1,2,4-thiadiazolyl, 1,3,4-thiadiazolyl, 1,2,5-thiadiazolyl, etc.) etc.; unsaturated condensed heterocyclo group containing 1 to 2 sulfur atoms and 1 to 3 nitrogen atoms (e.g., benzothiazolyl, benzothiadiazolyl, etc.) and the like. The term also embraces radicals where heterocyclo radicals are fused with aryl radicals. Examples of such fused bicyclic radicals include benzofuran, benzothiophene, benzopyran, and the like.

[0084] The term "alkylarylene" as used herein refers to a divalent radical derived from an aryl moiety (as defined herein) which is substituted with one or more alkyl groups by removal of a hydrogen atom from the aromatic moiety.

[0085] The term "alkylene-ether" as used herein means an alkylene group having at least one ether oxygen, such oxygen being either in-chain or being a terminal oxygen.

[0086] The term "arylene-ether" as used herein means an arylene group having at least one ether oxygen attached to the aryl group.
The term "organic solvent" as used herein refers to a carbon-based solvent, optionally containing heteroatoms, including, but not limited to, dichloromethane, tetrahydrofuran, ethanol, benzene, hexanes, DMF etc.

The term "organic base" as used herein is defined as any organic compound capable of deprotonating a selected compound of the present invention or forming a salt with an inorganic or organic acid and generally containing an amine moiety. Preferred "organic bases" of the present disclosure are secondary and tertiary amines, such as, triethylamine, diethylamine, or di-isopropyl-ethyl-amine etc.

The term "mineral base" as used herein refers to a basic substance that comprises an inorganic anion and cation, including, but not limited to, potassium carbonate or sodium carbonate.

The term "dynamic polymerization" as used herein refers to a method in which the monomeric units of an existing polymer are constitutionally exchanged with a different or new monomeric unit, optionally upon a substrate on which the existing polymer is coated. Generally, conditions sufficient for dynamic polymerization to occur are employed, such as heating the existing polymer with the new monomer, optionally in the presence of a catalyst. Dynamic polymerization also includes the re-polymerization of an existing polymer that has begun to decompose, similarly by employing conditions for dynamic polymerization. Dynamic polymerization can modify intrinsic opto-electronic properties of a polymer by undergoing constitutional component exchange. The opto-electronic properties include, but are not limited to, degree of polymerization, color, fluorescence, fluorescence color, and conductivity.

Further, the definitions and embodiments described in particular sections are intended to be applicable to other embodiments herein described for which they are suitable as would be understood by a person skilled in the art. For example, in the following passages, different aspects of the invention are defined
in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may be combined with any other feature or features indicated as being preferred or advantageous.

5 (II.A) AZOMETHINE AND ACYLHYDRAZONE POLYMERS

[0092] The present disclosure relates to azomethine and acylhydrazone polymers, which are optionally polymerized directly on substrates.

[0093] In one embodiment, the disclosure includes polymers of the formula

\[
\begin{align*}
&\text{H}_2\text{N} \left( \begin{array}{c}
R_1 \\
\text{N} \\
R_2 \\
\text{O} \\
R_3 \\
\text{n} \\
R_3
\end{array} \right) \\
&\text{R}_1 \text{ is alkylene, cycloalkylene, alkenylene, alkynylene, arylene, heteroarylene, NH-alkyl, NH-aryl, N(alkyl)alkyl, N(alkyl)-aryl, or } \text{NR}_4\text{C(0)}-\text{R}_4\text{C(0)NR}_4; \\
&\text{R}_2 \text{ is alkylene, arylene or heteroarylene;} \\
&\text{R}_3 \text{ is hydrogen, alkyl, aryl or heteroaryl;} \\
&\text{R}_4 \text{ is alkyl, aryl or heteroaryl;} \\
&\text{R}_5 \text{ is hydrogen, alkylene, arylene or heteroarylene; and} \\
&\text{n is an integer from 2 to 100,}
\end{align*}
\]

wherein the alkyl(ene), cycloalkyl(ene), alkenyl(ene), alkynyl(ene), aryl(ene) or heteroaryl(ene) groups are each optionally substituted with one to five substituents independently selected from halo, hydroxy, \text{CN, C(0)NH}_2, \text{C}_1\text{.}_\text{14}^-\text{alkyl, } \text{C}_3\text{.}_\text{C}_{10}^-\text{cycloalkyl, } \text{C(0)}\text{-aryl and -C(0)OR, or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to}
form a 5- or 6-membered ring, wherein \( R \) is H, \( \text{C}1-\text{C}6\)-alkyl (such as t-butyl) or aryl.

[0094] In another embodiment, \( R_1 \) is \( \text{C}1-\text{C}10\)-cycloalkylene, \( \text{C}2-\text{C}10\)-alkenylene, \( \text{C}2-\text{C}10\)-alkynylene, \( \text{C}6-\text{C}4\)-arylene, or \( \text{C}5-\text{C}14\)-heteroarylene, or \( R_1 \) is \( \text{C}5-\text{C}14\)-alkylene, \( \text{C}6-\text{C}4\)-arylene, or \( \text{C}5-\text{C}14\)-heteroarylene. In other embodiments, \( R_1 \) is selected from thiophenylene, phenylene, fluorene, and hexylene. In one embodiment, \( R_1 \) is selected from

\[
\begin{align*}
\text{Et}_2\text{C} & \quad \text{CO}_2\text{Et}, \\
\text{C}_6\text{C}_{13} & \quad \text{C}_6\text{C}_{13} \\
\text{and} & \\
\text{C}_6\text{C}_{13} & \quad \text{C}_6\text{C}_{13}
\end{align*}
\]

[0095] In another embodiment, \( R_2 \) is \( \text{C}5-\text{C}10\)-alkylene, \( \text{C}6-\text{C}4\)-arylene or \( \text{C}5-\text{C}14\)-heteroarylene. In one embodiment, \( R_2 \) is selected from

\[
\begin{align*}
\text{S} & \quad \text{O} \quad \text{O} \quad \text{C}_6\text{C}_{13} \\
\text{S} & \quad \text{O} \quad \text{O} \quad \text{C}_6\text{C}_{13} \\
\text{and} & \\
\text{S} & \quad \text{O} \quad \text{O} \quad \text{C}_6\text{C}_{13} \\
\text{S} & \quad \text{O} \quad \text{O} \quad \text{C}_6\text{C}_{13} \\
\text{and} &
\end{align*}
\]
In another embodiment, $R_3$ is hydrogen, $\text{Ci-C}_{-10}$-alkyl, $\text{Ce-Cu}$-aryl or $\text{Cs-Cl}_{4}$-heteroaryl, or hydrogen.

In certain embodiments, the polymer of the formula (I) is
wherein \( n \) is an integer from 2 to 100.

[0098] The disclosure also includes polymers having the formula (II)
R6 is as defined for R1 above,
R7 is as defined for R3 above; and
p is an integer from 2 to 100.

In another embodiment, the polymer of the formula (I) comprises a polymer of the formula (la)

wherein,
Ria is arylene or heteroarylene;
R2a is arylene or heteroarylene;
R3a is hydrogen or alkyl; and
r is an integer from 2 to 100;

wherein the aryl or heteroaryl groups are each optionally substituted with one to five substituents selected from halo, hydroxy, C1-alkyl, C3-Cio-cycloalkyl and - and C(0)OR, or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, and

wherein R is C1-C6-alkyl.

In another embodiment, one of R1a or R2a is a 9,9-di-substituted fluorene moiety of the formula (A)
wherein R' are each independently or simultaneously C\textsubscript{1-14}-alkyl or C\textsubscript{3-Cl\textsubscript{0}}-cycloalkyl, wherein the benzene rings of the fluorene monomer are optionally substituted with one to three substituents selected from halo, hydroxy, Cl\textsubscript{1-4}-alkyl, C\textsubscript{3-Cl\textsubscript{10}}-cycloalkyl and \textsubscript{C(0)OR}, or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, and wherein R is CrC\textsubscript{6}-alkyl.

[00101] In one embodiment, R\textsubscript{1a} is fluorene or thiophenylene. In another embodiment, R\textsubscript{1a} is

[00102] In another embodiment, R\textsubscript{2a} is fluorene or thiophenylene. In another embodiment, R\textsubscript{2a} is
In another embodiment, $R_{3a}$ is hydrogen.

In other embodiments, the polymer of the formula (la) is

PFI-co-Th, PFI-co-DAT or PFI-co-EDOT

5 (II.B) PROCESSES FOR PREPARATION OF AZOMETHINE AND ACYLHYDRAZONE POLYMERS

The polymers of the formula (I) and (II) are optionally directly prepared on a substrate. In one embodiment, the monomers which comprise the polymers of the formula (I) and (II) are coated on a substrate and then heated to a temperature sufficient for polymerization to occur.
[00106] In one embodiment, the monomers to prepare the polymers of the formula (I) and (II) are simply the corresponding diamine and di-aldehyde monomers which polymerize to form the polymer of the formula (I), and the corresponding amine-aldehyde monomers which polymerize to form the compound of the formula (II):

\[
\begin{align*}
\text{di-amine} & : \ H_2N - R_1 - NH_2 \\
di-aldehyde & : \ CO - R_2 \to CO - R_3 \\
\text{amine-aldehyde} & : \ H_2N - R_1 \to CO - R_3
\end{align*}
\]

[00107] In one embodiment, the monomers are coated on a substrate and heated to a temperature of about 50°C to about 200°C. In other embodiments, the substrate coated with monomers is heated for a time of about 2 minutes to about 120 minutes.

[00108] In another embodiment of the disclosure, the polymerization process to form polymers of the formula (I) and (II) are heated in the presence of a catalyst. The catalyst can be co-deposited on the substrate, or vaporized in the presence of the substrate. Examples of catalysts include, but are not limited to, organic acids such as trifluoroacetic acid, methane sulfonic acid, triflic acid; mineral acids such as sulfuric acid, hydrochloric acid and nitric acid; and Lewis acids such as boron trifluoride etherate.

[00109] Upon heating, optionally in the presence of a catalyst, the polymerization of the monomers occurs on the substrate, resulting in a substrate which is coated with a polymer of the formula (I) or (II). The pure polymers, which
are immobilized on the substrate, are obtained after rinsing with a solvent in which the monomers are soluble, thereby removing unreacted monomer.

[0010] Examples of substrate upon which the polymers of the formula (I), (Ia) and (II) are deposited include, but are not limited to glass, polyethylene terephthalate films, polymethylmethacrylate films, indium tin oxide coated glass, indium tin oxide coated polyethylene terephthalate films, transparent conductive oxide coated glass, transparent conductive oxide coated flexible plastic such as polyethylene terephthalate and polymethylmethacrylate.

(II.C) DYNAMIC POLYMERIZATION OF COMPOUNDS OF THE FORMULA (I) OR (II)

[0011] Dynamic polymerization allows for the manipulation of the existing opto-electronic properties (such as degree of polymerization, color, \( T_g \), molecular weight) of a polymer by exchanging a monomer in the polymer with a different monomer, as shown in FIGs. 1 and 2. Accordingly, the present disclosure includes a method for the dynamic polymerization of a polymer of the formula (I) and/or (II) in which an existing monomer in the polymer of the formula (I) and/or (II) is exchanged with a different monomer. Accordingly, the opto-electronic properties of the polymers of the formula (I) and (II) can be modified by using the method of the disclosure.

[0012] In one embodiment, the polymers of the formula (I) and/or (II) are capable of undergoing constitutional component exchange, or dynamic polymerization, in which the polymer of the formula (I) or (II) is contacted with a new monomer, and subsequently heated, to induce monomer exchange.

[0013] In one embodiment of the disclosure, there is included a method for the dynamic polymerization of a polymer of formula (I) or (II) as defined above, comprising:

(i) contacting the polymer of formula (I) or (II) with a compound of the formula (III), (IV) or (V):
(a) formula (III)

\[
\begin{align*}
\text{O} & \quad \text{O} \\
R_8 & \quad R_9 \\
\end{align*}
\]

wherein,
\( R_8 \) is as defined for \( R_2 \) above;
\( R_9 \) is as defined for \( R_3 \) above; and

(b) formula (IV)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{R}_{10} \quad \text{NH}_2 \\
\end{align*}
\]

wherein,
\( R_{10} \) is as defined for \( R_1 \) above;

(c) formula (V)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \text{R}_{11} \quad \text{R}_{12} \\
\end{align*}
\]

wherein,
\( R_{11} \) is as defined for \( R_1 \) above;
\( R_{12} \) is as defined for \( R_3 \) above; and

(ii) heating the polymer of the formula (I) or (II) with the compound of the formula (III), (IV) or (V) to a temperature sufficient for dynamic polymerization to occur. The dynamic polymerization results in a monomer of the formula (III), (IV) or (V) replacing a monomer as defined above (diamine; di-aldehyde, or amine-aldehyde) in the polymers of the formula (I) and/or (II). In another embodiment, a second, or third or more, dynamic polymerization can be conducted to further modify the opto-electronic properties of the polymer. Alternatively, more than
one monomer can be replaced with one or more different monomers at the same time.

[0014] In one embodiment, the dynamic polymerization is carried out on a coated substrate, in which the substrate is coated with a polymer of the formula (I) or (II). A compound of the formula (III), (IV) or (V) is then coated on the substrate, and the substrate heated to a temperature sufficient for dynamic polymerization to occur, optionally about 50°C to about 200°C. In other embodiments, the substrate is subjected to dynamic polymerization by heating for a time from about 2 minutes to about 120 minutes.

[0015] In another embodiment of the disclosure, the dynamic polymerization process is carried out in the presence of a catalyst. The catalyst can be co-deposited on the substrate, or vaporized in the presence of the substrate. Examples of catalysts include, but are not limited to, organic acids such as trifluoroacetic acid, methane sulfonic acid, triflic acid; mineral acids such as sulfuric acid, hydrochloric acid and nitric acid; and Lewis acids such as boron trifluoride etherate.

[0016] The polymers of the formula (I) and (II) are dynamic polymers whose properties can be altered through dynamic polymerization. For example, the color of the polymer of the formula (I) or (II) can be altered by contacting the polymer of the formula (I) or (II) with a monomer of the formula (III), (IV) or (V) followed by heat treatment, optionally in the presence of a catalyst, as described above. Accordingly, the dynamic polymerization provides the means to selectively control opto-electronic properties of a polymer, such as the color.

[0017] In another embodiment, the polymers of the formula (I) and (II) comprise self-healing polymers when coated on a substrate. For example, a polymer of the formula (I) and/or (II) will have a certain color, which when coated on a substrate may decompose over time, resulting in color fading. Accordingly, in one embodiment, the polymer of the formula (I) and/or (II) is restored by
repolymerizing by exposing the compound on the substrate to heat, which restores its given color for example.

(III) IMMOBILIZED CONJUGATED AZOMETHINE COMPOUNDS OF THE FORMULA (VI), (VII) AND (VIII)

[0018] Cross-linkable azomethines of the formula (VI) containing an acid sensitive oxetane are disclosed

![Structure of formula (VI)]

wherein:

(a) \( R_{13} \) is selected from the group consisting of CN, C(0)aryl, C(0)NH2 and CO2R18;

(b) \( R_{14} \) is selected from the group consisting of alkylene, ortho-arylene, meta-arylene, para-arylene, 1-alkylarylene, alkylene ether, and arylene ether;

(c) \( R_{15} \) is selected from the group consisting of H, alkyl, aryl, =CH and =C-alkyl, with the proviso that when \( R_{15} \) is =CH or =C-alkyl, the moiety \(-\text{NH-R}_{15}\) is \(-\text{N}=\text{R}_{15}\);

(d) \( R_{16} \) is selected from the group consisting of S, S0₂, O, NH, N-alkyl, N-aryl, N-SO2H, N-S0₂-alkyl and N-S0₂-aryl;

(e) \( R_{17} \) is selected from the group consisting of alkyl, O-alkyl, O-aryl, aryl, S-alkyl, S-aryl, N0₂, CN, and C0₂Rn; and
(f) R₈ is selected from the group consisting of H, alkyl, and monovalent organic or inorganic cations.

[0019] In one embodiment, R₁₃ is C₂₀₂Rn, wherein R₁₈ is dₕalkyl, such as methyl, ethyl or propyl, or R₄₈ is C₆₁oaryl such as phenyl, or R₁₃ is C(0)C₆₁oaryl, such as C(0)phenyl. In other embodiments, R₄₄ is C₁₄₄-alkylene, such as methylene or ethylene, or C₆₁o-arylene such as phenylene (ortho, meta or para). In certain embodiments, R₁₅ is H, C₁₄₄-alkyl (such as methyl or ethyl), or C₆₁oaryl such as phenyl. In one embodiment, R₁₈ is S, NH or 0. In one embodiment, R₁₆ is S. In other embodiments, R₁₇ is H, C₁₄₄alkyl, 0·C₁₄₄alkyl, 0·C₆₁oaryl. In one embodiment, R₁₂ is H.

[0020] In one embodiment, the compound of the formula (VI) is

![Chemical Structure Image]

[0021] The immobilization of an azomethine comprising the chemical structure of Formula (VI) on a substrate including, but not limited to, ITO glass electrodes can be catalytically done by cationic ring opening polymerization (CROP) of the oxetane group. CROP catalysts include, but are not limited to, organic acids such as trifluoroacetic acid, acetic acid, triflic acid, methanesulfonic acid, Lewis acids including, but not limited to BF₃-etherate, and mineral acids including, but not limited to sulphuric acid, hydrochloric acid, and nitric acid. The CROP catalyzed immobilization of the azomethine can be done by exposing films of the Formula (VI) to vapour of any of the said acids for prescribed times ranging from about 30 seconds to about 24 hours at room temperature or temperatures up to about 95°C.
Photoacid generators known to those skilled in the art, including, but not limited to bis-(4-fea-butyl-phenyl)-iodonium hexafluoroantimonate (Bu-Ph-l-Ph-BuSbF6), (9-oxo-9H-fluorene-2-yl)-phenyl-iodinium hexafluoroantimonate (Fl-l-PhSbF6), and diphenyliodonium 9,10-dimethoxyanthracene-2-sulfonate are suitable for the catalyzed CROP of the compound comprising the chemical structure of formula (VI). The photoacid generator is typically mixed at about 5 to about 10 weight % with the compound of formula (VI) in an organic solvent and then coated onto the substrate using spray coating or spin coating. Slot dye coating or ultrasound coating can also be used. The coating of the compound of Formula (VI) and the photoacid generator are irradiated with any discrete or mixture of wavelengths ranging from about 254 to about 500 nm for photoacid generation for CROP. Irradiation is typically done for about 0.5 to about 120 minutes, depending on excitation wavelength, film thickness, and photoacid generator. After exposure to either acid vapour or irradiation, the substrates coated with the compound of Formula (VI) are rinsed with, for example, dichloromethane with 10 % of triethylamine, or any other solvent that removes undesired materials such as unreacted starting materials and/or side products.

In an embodiment, the present disclosure relates to a method for the preparation of an azomethine compound of general Formula (VII). In an embodiment, the compound of general Formula (VII) comprises an acid sensitive group. In a further embodiment, the compound of general Formula (VII) comprises acid sensitive tert-butyl groups. Azomethines of general Formula (VII) are disclosed

wherein:
(a) $R_{19}$ is selected from the group consisting of CN, C(0)aryl, C(0)NH$_2$ and CO$_2$R$_{22}$;

(b) $R_{20}$ is an aryiene or heteroarylene;

(c) $R_{21}$ is selected from the group consisting of H, alkyl, aryl, =CH-alkyl, =CH-aryl, =C-alkyl, 1,4-benzyl-C0$_2$-tert-buty1, 1,3-benzyl-C0$_2$-tert-buty1, 1,2-benzyl-C0$_2$-tert-buty1, =CH-para-phenyl-C0$_2$-tert-buty1, 1,4-phenyl-C0$_2$-tert-buty1, =CH-ortho-phenyl-C0$_2$-tert-buty1, and =CH-mea-phenyl-C0$_2$-tert-buty1, with the proviso that when $R_{21}$ is =CH-alkyl, =CH-aryl or =C-alkyl, the moiety -NH-R$_{21}$ is $\equiv$N=R$_{21}$; and

(d) $R_{22}$ is selected from the group consisting of H, alkyl, tert-butyl and monovalent organic or inorganic cations.

[00124] In one embodiment, $R_{19}$ is CO$_2$R$_{11}$, wherein $R_{22}$ is C$_{1-14}$alkyl, such as methyl, ethyl, propyl, or t-butyl, or $R_{22}$ is C$_{6-10}$aryl such as phenyl, or $R_{19}$ is C(0)C$_6$-ioaryl, such as C(0)phenyl. In other embodiments, $R_{20}$ is Ce-u-arylene such as phenylene (ortho, meta or para) or fluorene (such as an unsubstituted or 9,9-di-C$_{1-14}$alkyl-substituted fluorene), Cs-ioheteroarylene, such as thiophenylene, pyrrole or furanylene. In one embodiment, $R_{20}$ is thiophenylene. In certain embodiments, $R_{21}$ is H, C$_{1-14}$-aryl (such as methyl or ethyl, up to decyl), or C$_{6-10}$-aryl such as phenyl, or benzyl, or 1,4-phenyl-C02-tert-buty1, 1,4-phenyl-C0$_2$H.

[00125] In one embodiment, the compound of the formula (VII) is
The solubility of azomethines comprising the chemical structure of Formula (VII) in organic solvents can be decreased with exposure to acids including organic, mineral, Lewis, and photoacid generators. Substrates coated with the compounds of Formula (VII) are exposed to the vapours of acids as mentioned above at room temperature or temperatures up to about 95 °C for typical times ranging from about 0.5 to about 18 hours. Coatings of the compound of Formula (VII) immobilized on substrates are obtained by rinsing the substrates with organic solvents including, but not limited to, dichloromethane, THF, ethanol containing 2-50 weight % of organic or mineral bases including, but not limited to, triethyl amine, diethyl amine, diisopropyl ethyl amine, potassium or sodium carbonate, or any other solvent that removes unwanted materials.

In an embodiment, a coating of the compound of Formula (VII) and the photoacid generator as mentioned above is irradiated with any discrete or
mixture of wavelengths ranging from about 254 to about 500 nm for photoacid generation CROP. Irradiation is typically done for about 0.5 to about 120 minutes depending on excitation wavelength, film thickness, and photoacid generator. After exposure to either acid vapor or irradiation, the substrates coated with the compound of Formula (VII) are washed with organic solvents such as dichloromethane, ethanol, or THF containing between 5 and 50 weight % of triethylamine, but can also include any organic or mineral base.

[00128] In another embodiment, the present disclosure relates to an electrochromic material of the polymer of the formula (I) which is of the Formula (VIII) wherein R23 is selected from the group consisting of CN, C(0)NH2, C(0)-aryl and CO2R25 wherein R25 is selected from the group consisting of ferf-butyl, H, alkyl and aryl; R24 is aryl; and m is from 2 to 50. In an embodiment of the present disclosure, the electrochromic material of general Formula (VIII) is obtained by thermally removing the heat-sensitive protecting group in a suitable organic solvent and depositing pre-polymers onto the electrode as described below. The electrochromic material is obtained by exposing the pre-polymer thin film (the coating described above) to a saturated atmosphere of organic, mineral or Lewis acid including, but not limited to, trifluoroacetic acid, triflic acid, methane sulfonylic acid, sulphuric acid, nitric acid, boron trifluoride etherate, boron tribromide, and heating the substrate at about 60 to about 150°C for about 0.25 to about 6 hours. The electrochromic material immobilized on the substrate is then rinsed with an organic solvent including, but not limited to, dichloromethane, THF, ethanol containing 2-50 weight % of organic or mineral bases including, but not limited to, triethyl amine, diethyl amine, diisopropyl ethyl amine and potassium or sodium carbonate to remove unreacted pre-polymer.

[00129] In an embodiment, the present disclosure relates to a polymer of Formula (VIII):
Structure of formula (VIII)

wherein:

(a) $R_{23}$ is selected from the group consisting of CN, C(0)NH$_2$, C(0)-aryl and CO$_2$R$_{25}$;

(b) $R_{24}$ is arylene or heteroarylene;

(c) $R_{25}$ is selected from the group consisting of tert-butyl, H, alkyl and aryl; and

(d) $m$ is from 2 to 50.

[00130] In one embodiment, $R_{23}$ is CO$_2$R$_{25}$, wherein $R_{25}$ is C$_{1-14}$alkyl, such as methyl, ethyl, propyl, or t-butyl, or $R_{25}$ is C$_{6-10}$aryl such as phenyl, or $R_{23}$ is C(0)C$_{6-10}$aryl, such as C(0)phenyl. In other embodiments, $R_{24}$ is C$_{6-14}$arylene such as phenylene (ortho, meta or para) or fluorene (such as an unsubstituted or 9,9-di-C$_{1-14}$alkyl-substituted fluorene), C$_{5-10}$heteroarylene, such as thiophenylene, pyrrolylene or furanlylene. In one embodiment, $R_{24}$ is thiophenylene or substituted thiophenylene, such as an ethylenedioxy-thiophenylene.

[00131] In one embodiment, the polymer of the formula (VIII) is
Films consisting of compounds of Formula (VI) and/or (VII) and polymers of the formula (VIII) are obtained by spin coating, spray coating, or drop casting from suitable solutions. Solvents for said solutions include but are not limited to, chloroform, dichloromethane, THF, ethanol, methanol, diethyl ether, chlorobenzene, toluene, xylene and o/tfro-dichlorobenzene, or mixtures thereof. In an embodiment of the present disclosure, the film thickness of the deposited azomethine layers ranges from about 10 nm to about 1000 nm. In a further embodiment of the present disclosure, the film thickness ranges from about 80 to about 200 nm.

In an embodiment, the present disclosure relates to an electrochromic device comprising an electrochromic layer prepared using compounds of Formula (VI) and/or (VII) and polymers of the formula (VIII). In an embodiment, the device is fabricated by coating an ITO coated glass slide with compounds of Formula (VI) and/or (VII) and polymers of the formula (VIII). The deposited layer is then immobilized using any one of the acid conditions described hereinabove. After rinsing, a conductive gel is deposited onto the immobilized layer using either spin or spray coating. An electrode is then deposited onto the gel and the device is baked at about 35° to about 65°C for up to about 120 minutes. The color of the azomethine electrochromic layer is switched upon applying a potential ranging from about 0.8 to about 3 V. The original color of the azomethine compound can be obtained by applying a potential ranging from about 0 to about -0.5 V.
Although the disclosure has been described in conjunction with specific embodiments thereof, if is evident that many alternatives, modifications and variations will be apparent to those skilled in the art. Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims. In addition, citation or identification of any reference in this disclosure shall not be construed as an admission that such reference is available as prior art to the present disclosure.

EXAMPLES

The operation of the disclosure is illustrated by the following representative examples. As is apparent to those skilled in the art, many of the details of the examples may be changed while still practicing the disclosure described herein.

Materials and Methods

Reagents and solvents from commercial sources were used as received unless otherwise stated. Anhydrous and deoxygenated solvents were obtained with an activated alumina column system. \(^1\)H and \(^{13}\)C NMR spectra were recorded at room temperature on a 400 MHz spectrometer. All the samples were dissolved in deuterated solvents and the spectra were referenced to the solvent line (CDCl\(_3\): \(^1\)H=7.26 and \(^{13}\)C=77.0 ppm) relative to TMS. CDCl\(_3\) for NMR polymer analyses was purified by repeatedly passing it over a plug of activated basic alumina.

Spectroscopic Measurements

Absorption measurements were done on a Cary-500 spectrometer and fluorescence studies were carried out on an Edinburgh Instruments FLS-920 fluorimeter after deaerating the samples thoroughly with nitrogen for 20 minutes in Precision Glass quartz cuvettes. Relative fluorescence quantum yields were measured at 10\(^{-5}\) M by exciting the corresponding compounds at its maximum absorption in spectroscopic grade 2-methylcyclohexane solutions at room
temperature relative to itself at 77 K under the same conditions. The slit widths and detector parameters were optimized for the fluorescence at 77 K. Absolute quantum yields were done at room temperature using an integrating sphere that was calibrated with fluorescein in ethanol with a calibrated excitation source. Quantum yields of the polymers in thin film were done at room temperature with the integrating sphere using a front face excitation/emission geometry. Thin films were prepared by spin coating THF solutions of the given polymer onto thin glass microscope slides.

Polymer doping was done in dichloromethane (10^{-5} M) with stock solutions of FeCl₃ and hydrazine that were sequentially added (5 \mu L). The resulting absorbance spectra after the addition of the dopant and reductant were subsequently recorded. Similarly, stock solutions of trifluoroacetic acid (TFA) and triethylamine (TEA) were sequentially added (5 \mu L) to the given polymer solution and the resulting absorbance spectra were recorded. The oxidation stoichiometry with FeCl₃ was determined via the Job method using stock solutions of known mole fractions (1.0 mM) of the polymer and ferric chloride.

**Electrochemical Measurements**

Cyclic voltammetry measurements were performed on a Bio Analytical Systems EC Epsilon potentiostat. Compounds were dissolved in anhydrous and deaerated dichloromethane at 10^{-4} M with 0.3 M TBAF. A platinum electrode and a saturated Ag/AgCl electrode were used as auxiliary and reference electrodes, respectively.

**Molecular Weight Measurements**

GPC analyses were done with a Breeze system from Waters equipped with a 717 plus autosampler, a 1525 Binary HPLC pump and a 2410 refractive index detector. Three Styragel™ columns HR3, HR4 and HR6 (7.8 x 300 mm) in series were used for resolving the different samples. The flow rate of the THF eluent was 1 mL/min. The temperature of the columns was 33°C.
Molecular weights were calculated relative to polystyrene standards with a SM-105 kit of 10 molecular weight standards from Shodex.

**Thermal and Calorimetric Analyses**

Thermogravimetric analyses (TGA) studies were carried out on a Hi-Res TGA 2950 thermogravimetric analyser (TA Instruments) with a 10°C/minute ramp to 700°C ($T_{\text{dec}}$ was defined as the onset of the decomposition temperature). Differential scanning calorimetry (DSC) studies were carried out on a TA instrument with a 5°C/minute ramp from -50 to 220°C under both N$_2$ and ambient atmosphere.

**Example 1a - Polymerization**

![Chemical structure](image)

Equimole amounts of diethyl 2,5-diaminothiophene-3,4-dicarboxylate and 2,5-thiophene dicaaroaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is blue.

**Example 1b**
Equimole amounts of diethyl 2,5-diaminothiophene-3,4-dicarboxylate and 2,3-dihydrothieno[3,4-b][1,4]dioxide-5,7-dicarbaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is blue.

Example 1c

Equimole amounts of diethyl 2,5-diaminothiophene-3,4-dicarboxylate and terephthalic dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is red.

Example 1d
Equimole amounts of diethyl 2,5-diaminothiophene-3,4-dicarboxylate and isoterephthalic dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is orange.

Example 1e

Equimole amounts of diethyl 2,5-diaminothiophene-3,4-dicarboxylate and 2,7-fluorene dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is orange.

Example 1f
Equimole amounts of diethyl 2,7-diaminofluorene and 2,7-fluorene dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is yellow.

Example 1g

Equimole amounts of diethyl 2,5-diaminothiophene-3,4-dicarboxylate and 9,9-dimethyl-2,7-fluorene dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is yellow.

Example 1h
Equimole amounts of diethyl phenylene diamine and 2,5-thiophene dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is orange.

Example 1i

Equimole amounts of hexamethylene amine diamine and 2,5-thiophene dicarboxaldehyde were dissolved in dichloromethane (2 mL) in a concentration of 2 mg/mL. A catalytic amount of trifluoroacetic acid was added to the solution and the homogeneous mixture was spray coated onto the desired substrate. The substrate was then heated at 60°C in a trifluoroacetic acid saturated atmosphere for 0.5 hrs. The substrate was then rinsed with a 10 weight % solution of triethylamine in dichloromethane. The resulting polymer is orange.

Example 2a - Dynamic Polymerization

To any of the polymers 8, 9, 10 and 13 coated on a substrate is coated with 2,5-thiophene dicarboxaldehyde. The substrate is then heated to 75 °C for 10 minutes in a trifluoroacetic acid saturated atmosphere. The substrate is then cooled and rinsed with dichloromethane containing between 5 and 35 weight % triethylamine to afford polymer 6 with n equal to at least 10.

Example 2b

To any of the polymers 8, 9, 10, 13 and 14 coated on a substrate is co-coated with 2,5-thiophene dicarboxaldehyde containing between 1 to 10 mole % of trifluoroacetic acid. The substrate is then heated to 75 °C for 10 minutes. The
substrate is then cooled and rinsed with dichloromethane containing between 5 and 35 weight % triethylamine to afford polymer 6 with n equal to at least 10.

Example 2c

To the polymer 15 (to give 14) and 16-17 (to give 6) that is coated on a substrate is coated with 2,5-diaminothiophene-3,4-dicarboxylate. The substrate is then heated to 75 °C for 10 minutes. The substrate is then cooled and rinsed with dichloromethane to afford polymer 14 or 6 with n equal to at least 10.

Example 2d

To polymer 15 (to give 14) and 16-17 (to give 6) that is coated on a substrate is co-coated with 2,5-diaminothiophene-3,4-dicarboxylate containing between 1 to 10 mole % of trifluoroacetic acid. The substrate is then heated to 75 °C for 10 minutes. The substrate is then cooled and rinsed with dichloromethane containing between 5 and 35 weight % triethylamine to afford polymer 14 or 6 with n equal to at least 10.

Example 3 - Conjugated fluorescent azomethine copolymers of the formula (la)

Syntheses

[00142] The monomers 9,9-dihexyl-fluorene-2,7-diamine (1), 9,9-dioctyl-fluorene-2,7-dicarbaldehyde, diethyl 2,5-diaminothiophene-3,4-dicarboxylate, and
2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde were synthesized according to previously reported procedures. Similarly, PFI-co-FI was prepared according to known methods.

**Example 3a - 3-(2-Ethylhexyl) thiophene**

In anhydrous THF (50 mL) was dissolved magnesium (2.65 g, 109 mmol) and 2-ethylhexyl bromide (15 g, 77 mmol). The reaction mixture was stirred for 30 min at 0 °C. The temperature was then gradually warmed to room temperature until most of the magnesium reacted, followed by refluxing for 2 h. In another flask was dissolved 3-bromothiophene (7.0 g, 43 mmol) to which was then added [1, 3-bis (diphenylphosphino) propane] nickel (II) chloride (200 mg, 0.4 mmol) in anhydrous THF (100 mL). Three cycles of freeze-pump-thaw were performed to ensure complete removal of oxygen. The prepared 2-ethylhexyl magnesium bromide Grignard reagent was added by cannula to the red coloured solution of nickel catalyst and the resulting brown solution was then refluxed for 18 hours. The reaction mixture was washed with aqueous HCl (10 % w/w) after cooling to room temperature. The organic phase was extracted with ethyl acetate, dried with MgSO₄, and the solvent was evaporated after removing the MgSO₄. The crude product was chromatographed on silica with 100 % hexanes to afford a colourless oil (4.9 g, 58 %). ¹H-NMR (CDCl₃): δ= 7.23 (d, 1H), 6.94 (d, 2H), 2.53 (t, 2H), 1.44 (m, 1H), 1.30 (bs, 8H), 0.91 (t, 6H).

**Example (3b) - 3-(2-Ethylhexyl) thiophene-2,5-dicarbaldehyde (5):**

To a solution of 3-(2-ethylhexyl) thiophene (7.5 g, 38 mmol) and freshly distilled TMEDA (9.8 g, 84 mmol) diluted in anhydrous hexanes (50 mL) under nitrogen, was added drop-wise a solution of 2 M n-BuLi in hexane (42 mL, 84 mmol). After refluxing for 1.5 hours, THF (40 mL) was added and the solution was cooled to -50 °C. Anhydrous DMF (14 mL, 190 mmol) was then added drop-wise, after which the reaction mixture was allowed to warm to room temperature. After 2.5 h at room temperature, the reaction mixture was hydrolyzed with water
(60 mL) and the mixture was extracted with ether. The organic layers were dried over MgSO\textsubscript{4} and concentrated. The crude product was purified by column chromatography with hexanes/ethyl acetate (90/10 v/v) to give the product as a colorless oil (5.8 g, 61 %). \textsuperscript{1}H-NMR (CDCl\textsubscript{3}) \( \delta \) ppm: 10.09 (s, 1H), 9.56 (s, 1H), 7.16 (s, 1H), 2.61 (t, 2H), 1.59 (septet, 1H), 1.31 (qt, 2H), 1.04 (bs, 6H), 0.92 (t, 6H). HR-MS(+) calculated for [C\textsubscript{14}H\textsubscript{20}O\textsubscript{2}S+H]\textsuperscript{+}: 253.12; found: 253.12.

**Example (3c)** - Polv(3-(2-ethyl-hexyl)-thiophene)-co-9,9-dihexyl-fluorenylazomethine (PFI-co-Th):

The copolymerization was done by mixing 1 (100 mg, 0.27 mmol) and 3-(2-ethyl-hexyl)-thiophene-2,5-dicarbaldehyde (68 mg, 0.27 mmol) in CHCl\textsubscript{3} (3.0 mL) in a pressure tube. A catalytic amount of diluted TFA (30 \( \mu \)L) was then added. The pressure tube was sealed and heated to 90 °C for 48 h. The reaction mixture was cooled to room temperature and the polymer was precipitated from a methanol/water mixture. The resulting red solid (60 %, 80 mg) was filtered and washed with methanol, water and acetone and then dried under vacuum overnight. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) ppm: 10.41 (m, CHO), 8.95 (m, -N=CH-), 8.40 (s, -Th-H) 7.34-7.71 (m, Fl-H), 6.71 (b, NH\textsubscript{2}), 2.82 (m, -CH\textsubscript{2}), 1.31 (m, -CH-CH\textsubscript{2}-), 1.93 (m, -CH\textsubscript{2}), 0.77 (m, -CH\textsubscript{3}).

**Example (3d)** - Poly(thiophene-3,4-dicarboxylic acid diethyl ester)-cc~9,9-dioctyl-fluorenylazomethine (PFI-co-DAT):

The copolymerization was done similar to that above with 1 (485 mg, 1.88 mmol) and 9,9-dioctyl-fluorene-2,7-dicarbaldehyde (840 mg, 1.88 mmol) in CHCl\textsubscript{3} (10 mL) in a pressure tube. The title polymer was isolated as a red solid (70 %, 120 mg). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \( \delta \) ppm: 10.1 (m, CHO), 8.52 (m, -N=CH-), 7.53-7.91 (m, Fl-H), 6.35 (b, NH\textsubscript{2}), 4.24-4.49 (m, O-CH\textsubscript{2}), 2.02 (m, -CH\textsubscript{2}), 1.33 (m, -CH\textsubscript{2}-CH\textsubscript{2}-), 0.80 (m, -CH\textsubscript{2}-), 0.59 (m, -CH\textsubscript{3}).

**Example (3e)** - Polv(2,3-dihydro-thieno[3A-biri,41dioxine)-co-9,9-dihexyl-fluorenylazomethine (PFI-co-EDOT)
The copolymerization was similar to that above with 2,3-dihydrothieno[3,4-b][1,4]dioxine-5,7-dicarbaldehyde (163 mg, 0.882 mmol) and \( \text{Th-FI-Th} \) (300 mg, 0.882 mmol) in CHCl\(_3\) (6 ml) in a pressure tube. The title polymer was isolated as a red solid (60 %, 140 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) ppm: 10.01 (m, CHO), 8.75 (m, -N=CH-), 7.31-7.71 (m, Fl-H), 6.7 (b, NH\(_2\)), 4.44-4.47 (m, O-CH\(_2\)), 1.99 (m, -CH\(_2\)), 1.05 (m, -CH\(_2\)-CH\(_2\)-), 0.78 (m, -CH\(_3\)), 0.64 (m, -CH\(_3\)).

**Example (3f)** - 9,9-Dihexyl-11,N'-bis-thiophen-2-ylmethylene-fluorene-2,7-diamine (Th-FI-Th)

In ethanol (20 ml) were dissolved \( \text{Th-FI-Th} \) (40.0 mg, 0.1 mmol) and thiophene-2-carbaxyldehyde (36 mg, 0.32 mmol) to which was then added a 1 M solution of TFA (20 \( \mu \)L). The solution was stirred at room temperature for 12 h, after which the solvent was evaporated and the product was extracted into ethyl acetate. The organic layer was washed with a brine solution and dried over Na\(_2\)SO\(_4\). After filtering, the solvent was removed under reduced pressure and the crude product was purified by silica gel column chromatography with hexanes/ethyl acetate (80/20 v/v). The product was obtained as an orange solid (32 mg, 58% yield). \(^1\)H NMR (CDCl\(_3\)) \( \delta \) ppm: 8.7 (s, 2H), 7.68 (d, 2H), 7.53 (d, 4H), 7.23-7.29 (m, 4H), 7.01 (s, 2H), 1.99 (t, 4H), 1.25 (p, 4H), 1.11 (m, 4H), 0.78 (t, 6H), 0.66 (t, 4H). \(^{13}\)C NMR (acetone) \( \delta \) ppm: 164.9, 164.3, 161.5, 147.0, 144.1, 140.4, 133.4, 131.0, 102.2, 61.1, 60.1, 32.2, 32.0, 26.7, 22.9, 14.4, 14.1, 13.9. HR-MS (+) calculated for \([\text{C}_{35}\text{H}_{44}\text{O}_{2}\text{S}_2 + \text{H}]^+\) 522.84, found 522.81.

**Example (3a)** - 9,9-Dihexyl-N,N'-bis-(5-butyl-thiophen-2-ylmethylene)-fluorene-2,7-diamine (Th-FI-Th?)

In ethanol (40 ml) were dissolved \( \text{Th-FI-Th} \) (110.0 mg, 0.41 mmol) and 5-butyl-thiophene-2-carbaxyldehyde (222 mg, 1.32 mmol) to which was then added a 1 M solution of TFA (60 \( \mu \)L). The solution was stirred at room temperature for 12 h. The solvent was then removed under reduced pressure and the crude
product was extracted into ethyl acetate. The organic layer was washed with a brine solution and dried over Na₂SO₄. After filtering and then removing the solvent under reduced pressure, the crude product was purified by silica gel column chromatography with hexanes/ethyl acetate (70/30 % v/v). The product was obtained as an orange solid (212 mg, 78% yield). ¹H NMR (acetone-d₆) δ ppm: 8.78 (s, 2H), 7.78 (d, 2H), 7.46 (d, 2H), 7.37 (d, 2H), 7.25 (d, 2H), 6.94 (d, 2H), 2.88 (t, 4H), 1.73 (p, 4H), 1.30 (t, 4H), 1.08 (p, 8H), 0.95 (t, 6H), 0.74 (t, 12H). ¹³C NMR (acetone) δ ppm: HR-MS (+) calculated for [C₄₃H₅₆N₂S₂ + H]⁺ 665.05, found 665.1

Discussion

[00149] The copolymers of the formula (la), for example those in Scheme 1, were prepared to examine the opto-electronic characterization of the compounds. It was expected that the HOMO-HOMO energy-gap could be tailored by incorporating different electron rich and deficient moieties, such as thiophenes, resulting in emissions covering the RGB primary colors. Similar to emission color tailoring, the oxidation potential was also expected to be modulated contingent on the electron richness of the thiophene units in addition to the placement of the azomethine nitrogen.
The compound polymers of the formula (la) presented in Scheme 1 were targeted for examining the effect of incorporating different groups, such as thiophenes, on the polymer's opto-electronic properties. The particular properties of interest were the emission colors and fluorescence quantum yields, given that previously investigated polyazomethines were all non-fluorescent. The exception is PFI-co-FI that fluoresces in appreciable amounts (Table 1). The additional benefit of incorporating groups such as thiophene into the polymers is that significant spectral changes for both the absorbance and emission are expected relative to the all-fluorene PFI-co-FI polymer. Significant spectral changes are additionally expected between PFI-co-Th vs. PFI-co-EDOT, owing to the electronic differences of the EDOT and thiophene moieties. Meanwhile, the effect of the azomethine placement on the opto-electronic properties is
expected by comparing the measured properties of PFI-co-DAT relative to both PFI-co-Th and PFI-co-EDOT.

The monomers required for synthesizing the targeted copolymers were prepared by known means. Notably, the diaminothiophene was prepared in one-step from elemental sulfur via the Gewald reaction. Meanwhile, the diaminofluorene (1) was prepared in three steps in 72% overall yield starting from fluorene (Scheme 2). It is noteworthy that the resulting 1 is not stable under ambient conditions for extended periods of time. It was therefore immediately polymerized once it was obtained in high purity. The complementary fluorene-2,7-dicarboxaldehyde (2) was prepared from 2,7-dibromofluorene in two steps in 58% overall yield (Scheme 2). The 3-(2-ethylhexyl)thiophene derivative was prepared from 3-bromothiophene via the Kumada reaction. This monomer was chosen over 3,4-dialkylated thiophenes because the resulting polymer was expected to be soluble. Moreover, its preparation gives rise to fewer side products, in contrast when starting with 3,4-dibromothiophene.
Synthetic route for selected monomers: (i) DMSO, 50% NaOH, 1-bromohexane, rt, 4 d, (ii) HN\textsubscript{3}, reflux, 2 h, (iii) THF/EtOH, 10% Pd/C, reflux, hydrazine monohydrate, rt, overnight, (iv) THF, Bu-Li, -78 °C, DMF, rt, overnight, (v) DMF, Et\textsubscript{3}N, rt, (vi) Mg, THF, 1-bromo-2-ethylhexyl, Ni(dppp)\textsubscript{2}, 80 °C, 16 h.

Scheme 2

[00152] The targeted polymers were prepared by combining stoichiometric amounts of the given monomers in chloroform in addition to a catalytic amount of trifluoroacetic acid. The homogeneous reaction mixture was subsequently heated to 90 °C in a sealed pressure tube for 48 hours. In all cases, the polymers were red in color, confirming their increased degree of conjugation relative to their colorless monomers. While highly pure polymers could be obtained by simple removal of the solvent, the polymers were precipitated from a methanol/water mixture. This was to ensure that undesired low molecular weight oligomers and monomers, that would otherwise influence the opto-electronics
properties, were removed. The targeted polymers were obtained in both good yields and high purity after precipitation (Scheme 3).

![Scheme 3](image)

5 Both $^1$H-NMR and GPC were used for confirming polymer formation. While formation of the desired azomethine is inferred by the change in color during the polymerization owing to an increase degree of conjugation, absolute confirmation was possible by $^1$H-NMR. The azomethine proton has a distinctive chemical shift at ca. 8.5 ppm that does not overlap with other protons. This provides a clean window for accurate integration relative to the chain-end aldehyde, which also has a distinct resonance at ca. 10 ppm. The average
degree of polymerization (DPₙ) was calculated by integrating imine protons relative to the terminal aldehydes. The average Mₙ calculated by NMR was consistent with that determined by relative GPC calibrated against polystyrene standards. The measured molecular weights and thermal properties are summarized in Table 2. While there is an appreciable difference in the degree of polymerization of PFI-co-DAT relative to PFI-co-Th and PFI-co-EDOT, this was not expected to impact the opto-electronic properties. This is based on previous work with polythiophene azomethines that showed no change in opto-electronic properties with DPₙ > 10.

The thermal properties of the polyfluorenylazomethines were investigated by both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Interestingly, no weight loss was seen at 100 °C, confirming that the polymers are not hydroscopic and that the azomethine is not as a hydrate. This is contrast to the all-thiophene polyazomethine that was hydroscopic. All the polymers investigated similarly showed resolvable glass transition temperatures (Tₛ) between 115 ° and 148 °C, as seen in the inset of Fig. 3. PFI-co-Th has the lowest Tₛ as result of the branched 2-ethylhexyl side chain. Meanwhile, both PFI-co-DAT and PFI-co-EDOT were found to have similar Tₛ, despite having different DPₙ.

Discussion - Photophysical Properties

Both the absorbance and fluorescence properties of the polyazomethines were investigated. As seen in Fig. 4, there are appreciable differences in the spectra that are dependent on the type of thiophene incorporated into the polymer. Taking PFI-co-FI as the benchmark (λₘₐₓ = 450 and λᵣ = 560 nm),
both the absorbance and fluorescence of the thiophene copolymers are bathochromically shifted. This is a result of the electron richness of the heterocycle. Also, it is known that heterocycles adopt coplanar arrangements with the azomethine bond to which they are attached. This further increases the degree of conjugation leading to the observed spectral changes. This is in contrast to homoaryls that are twisted by up to 65° from the azomethine bond to which they are attached. Therefore, increased degrees of conjugation inherently occur with heterocyclic azomethines.

The absorbance of PFI-co-DAT is red shifted by 40 nm from PFI-co-EDOT, which in turn is red shifted by 60 nm from PFL-co-Th. The bathochromic shifts are a result of electronic effects. For example, the electron donating effect of the EDOT moiety works in concert with the electron withdrawing azomethine. The net result is an electronic push-pull effect. The bathochromatic shift is more pronounced with PFI-co-DAT owing to the electronic pull-pull effect between the electron withdrawn esters and azomethines. The trend of bathochromic shifts is also observed with the fluorescence spectra shown in Fig. 4B. The effect of the different thiophenes on the optical properties is further evident in the photographs in Fig. 5. While subtle variations in color are visibly seen in the absorbance, the effect is more pronounced in the fluorescence. As seen in panels D-F of Fig. 5, the three primary red, blue, and green emission colors are possible contingent on the thiophene incorporated into the copolymer.

Bathochromic shifts were also seen with spin coated samples of the polyazomethines deposited as thin films. This is in part owing to increased π-
stacking in the solid state. The thin film absorbance spectra are bathochromically shifted by ca. 20 nm while the fluorescence spectra are shifted by about 70 nm from the corresponding polyazomethine in solution.

[00158] The property of particular interest for the polyazomethines is their fluorescence quantum yield (\(\Phi_f\)). This is because the azomethine linkage is known to quench the fluorescence of even the most intrinsically fluorescent fluorophores.\(^{33}\) The desired fluorescence quantum yields were measured using an integrating sphere. This method is preferred over relative methods because the absolute quantum yields can be measured independent of references whose fluorescence yields are wavelength dependent and typically contain errors up to 20%. The \(\Phi_f\) can therefore be accurately determined.

[00159] As seen in Table 1, the polymers fluoresce in considerable amounts. In fact, the \(\Phi_f\) are comparable to polyfluorene vinylenes that are used in emitting devices. This is in contrast to previously investigated thiophene azomethine derivatives whose fluorescence quantum yields were ca. 0.01. Analogous copolyazomethines derived from 9,9-unsubstituted 2,7-diaminofluorene also do not fluoresce.\(^{2,34}\) As seen in the photographs D-F in Fig. 5, the polymer fluorescence can visually be detected by the naked eye. The less intense emission seen in Fig. 5 (F-G) is from the poor photo response of the camera’s PMT and not from a low fluorescence yield. This is supported by the absolute \(\Phi_f\) of the polymers that are all on the order of 10%. High \(\Phi_f\) were even observed in thin films, suggesting that there is little self-quenching. The measured absolute fluorescence quantum yields when compared to previously reported studies, confirm that 9,9-dialkylation of the diaminofluorene is a structural element which preserves the inherent fluorescence of the fluorene.

[00160] While the polymers' \(\Phi_f\) are ca. 10%, their fluorescence could be restored to near unity by two means; low temperature and acid doping. Reducing the temperature to 77 K resulted in fluorescence yield enhancement. It
should be noted that the calculated values at 77 K are uncorrected for the change in solvent refractive index with temperature. Therefore, the measured values are lower limits and the true amount of fluorescence enhancement is expected to be 20% higher. Nonetheless, the increased fluorescence with temperature implies that reduced fluorescence at room temperature most likely involves bond rotation deactivation processes.

[00161] Similar to the temperature induced fluorescence changes, fluorescence enhancement was also possible by protonating the azomethine with trifluoroacetic acid. Meanwhile, their fluorescence enhancement with temperature and protonation illustrate the sensor-like properties of polyazomethines.

[00162] The thiophene-fluorene triads (Th-Fi-Th and Th-Fi-Th₂ seen in Scheme 1) were prepared to investigate whether high $\Phi{_e}$ were also possible with triads derived from 1 and having reduced degrees of conjugation relative to their polymer counterparts. Equally high $\Phi{_e}$ were observed with the model compounds. They similarly exhibited the same fluorescence enhancement at low temperature and with acid protonation. The collective spectroscopic data confirm that both the color and emission of fluorescence can be tailored as a function of the thiophene. Also, fluorescent alternating copolyazomethines that emit with the primary RGB colors are possible by adjusting the HOMO-LUMO energy levels.

Discussion - Electrochemistry

[00163] The electrochemical properties of the polymers were investigated by cyclic voltammetry to further gain insight into structural effects on the oxidation potential ($E_{pa}$). As seen in Fig. 6, the polymers all undergo an oxidation process. Both the $E_{pa}$ and the reversibility of the anodic process are contingent on the thiophene. For example, the $E_{pa}$ of PFI-co-EDOT is less positive than PFI-co-Th by 130 mV, as expected owing to the strong electron donating character of EDOT. Meanwhile, the $E_{pa}$ of PFI-co-DAT is 70 mV higher than PFI-co-Th. The
increased $E_{pa}$ is expected given the strong electron withdrawing character of the thiophene esters. The measured $E_{pa}$ of the polyazomethines confirms that the polymers are stable under ambient conditions. Meanwhile, the reversible oxidation for both PFI-co-Th and PFI-co-EDOT confirms the robustness of the heteroatomic bond under oxidation conditions.

[00164] The polymers also underwent cathodic processes corresponding to a two-electron transfer. The reduction potential ($E_{pc}$) was less affected by the thiophene incorporated into the copolymer than the corresponding $E_{pa}$. Only in the case of PFI-co-EDOT (Fig. 7) was the cathodic process reversible.

[00165] The electrochemistry of the Th-Fi-Th triads was also investigated. Comparing their $E_{pa}$ to that of PFI-co-Th would provide insight into the effect of the degree of conjugation on the oxidation potential. Furthermore, comparing the anodic behaviour of Th-Fi-Th$_2$ relative to Th-Fi-Th$_1$ would provide information about both the stability of the radical cation and the azomethine bond. The $E_{pa}$ of both Th-Fi-Th was 80 mV more positive than the corresponding polymer. While the electron withdrawing character of the azomethine should increase the oxidation potential, the high degree of conjugation of PFI-co-Th offsets this effect, leading to the observed less positive $E_{pa}$. As expected, there is a noticeable difference between the reversibility of the oxidation process of Th-Fi-Thi and Th-Fi-Th$_2$. The oxidation process of Th-Fi-Th$_2$ was reversible while that of Th-Fi-Thi was pseudo-reversible. The $\alpha,\alpha'$ alkylation of Th-Fi-Th$_2$ prevents the electrochemically generated radical cation from coupling according to known means. The observed reversible oxidation confirms that the azomethine is robust. It further confirms that heteroatomic bond does not decompose when oxidized. Meanwhile, the pseudo-reversible oxidation of Th-Fi-Thi suggests that the radical cation is not highly reactive. This is most likely a result of the high degree of conjugation of the compounds allowing the radical cation to be delocalized across the entire molecule.
The spectroscopic properties of the electrochemically generated radical cation were additionally investigated by spectroelectrochemistry. This was done by applying a potential slightly more positive than the $E_{pa}$ of the given polymer and observing the resulting absorbance changes. In all cases, the absorbance of the generated radical cation was bathochromically shifted from the corresponding neutral form (Table 1). The most stark visible color change was with PFI-co-DAT, whose color changed from red to blue upon oxidation. This is seen in the inset of Fig. 6. The new absorbance occurred at 620 nm while the absorbance of the electrochemically generated radical cation for PFI-co-Th and PFI-co-EDOT was 442 and 450 nm, respectively. The original color of the polymers could be quantitatively restored by applying a potential of -100 mV. This once again illustrates the robustness of the polyazomethines.

**Discussion - Halochromism and Chemical Oxidation**

Given that electrochemically induced color changes were possible, the chemical doping of the polymers was additionally investigated. Oxidizing the polymers in solution has the advantage that the stability of the doped state can be assessed by monitoring the reversible color changes. This is in contrast to the spectroelectrochemical studies where diffusion does not occur and the intermediates are artificially stable. Dichloromethane solutions of the copolymers were oxidized with FeC^+. This is a choice oxidant because it is spectroscopically transparent in the spectral window investigated. Its reduction potential is also compatible with the oxidation potentials of the polymers investigated.

Significant color changes occurred upon adding the oxidant and the resulting absorbance shifts are summarized in Table 1. A representative absorbance spectral change of PFI-co-EDOT is shown in Fig. 8, illustrating a 50 nm bathochromic shift in the absorbance upon chemical doping. The oxidized species were subsequently neutralized to the original state after equilibrating for a few minutes and by adding excess hydrazine hydrate. The reversible color changes between the neutral and oxidized states are seen in the pictures of Fig.
Both the original intensity and absorbance of the neutral azomethines were observed when reducing the oxidized states with hydrazine hydrate. It should be noted that no special precautions such as anhydrous or degassed solvents were used for the oxidation/neutralization studies. Hypsochromic shifts, decrease in intensity, and even complete disappearance of the absorbance would be observed if the polyazomethines decomposed or hydrolyzed during the oxidation/neutralization cycle. The absence of detectable change in the absorbance spectra between the original and the oxidized/neutralized azomethines (Figs. 8 and 9) confirm the azomethines are both hydrolytically and oxidatively robust. The exception is PFI-co-DAT that undergoes some decomposition, which is consistent with the electrochemical studies (vide supra).

The added advantage of oxidation studies in solution is that the stoichiometry can be spectroscopically determined via the Job method. By varying the mole fraction of the oxidant, the stoichiometry can be derived from the absorbance maximum, as seen in the inset of Fig. 8. A 1:1 stoichiometry was found for all the compounds in Scheme 1. Given that ferric chloride is a one-electron oxidant, taken together with the determined stoichiometry, the chemically generated intermediate is a radical cation. This is consistent with the electrochemically produced species measured by cyclic voltammetry.

Azomethines are known to be halochromic with significant spectral changes occurring when protonated. The advantage of the studied polyazomethines is that they absorb strongly in the visible as a result of their extended degree of conjugation. Therefore, their protonation should lead to significant visible color changes. This provides the means to spectroscopically follow the stability of the protonated form and to investigate their resistance towards acid hydrolysis. The halochromic behaviour (color change with protonation) of the azomethines in Scheme 1 was subsequently investigated with trifluoroacetic acid. Exposing the polyazomethines to concentrated acid resulted in absorbance bathochromic shifts. However, the acid induced spectral changes
were less pronounced than those observed with ferric chloride. This is owing to the resulting cation that has weaker charge transfer than the radical cation that is produced by oxidation.

[00171] The protonated azomethines could be neutralized by adding triethylamine. Similar to the oxidation studies, the azomethines could be reversibly protonated and neutralized without any spectroscopically detectable decomposition. The exception being PFI-co-DAT that undergoes minor color degradation. The reversible protonation/neutralization is illustrated in Fig. 8. The salient features of the absorbance spectrum are the reversible color change without color degradation after protonation and neutralization. Given that anhydrous solvents or special precautions were not used for the halochromic studies, residual water in the solvent or ambient moisture would readily hydrolyze the azomethine bond upon acid addition. However, no color degradation was observed after protonation/neutralization cycles. This demonstrates the resistance of the azomethines towards acid hydrolysis. The collective halochromic and oxidation spectroscopic studies confirm that the conjugated azomethine derivatives are robust and they resist both oxidation and acid hydrolysis.

*Example 4 - Azomethine compounds of the Formula (VI), (VII) and (VIII)*

A general procedure for preparing compounds of the Formula (VI) is shown in Scheme 4:
(i) p-TsCl, 5N-NaOH, THF, rt; (ii) 4-(Thiophen-3-yl)-phenol, K$_2$CO$_3$, DMF, 75 °C, 16 h; (iii) TMEDA, Bu-Li, hexane, -78°C, THF, DMF, 4-16 h; (iv) 2,5-Diamino-thiophene-3,4-dicarboxylic acid diethyl ester, TFA, EtOH, rt, 16 h; (v) NBS, CHCl$_3$:AcOH (1:1), rt, 16 h; (vi) Toluene-(4-sulfonic acid 3-methyl-oxetan-3-yl) methyl ester, KOH, THF, reflux, 16 h.

SCHEME 4
Example (4a) - Toluene-(4-sulfonic acid 3-methyl-oxetan-3-yl) methyl ester.

[00172] In THF (50 mL) was dissolved (3-methyl-oxetan-3-yl)-methanol (5.0 g, 48.95 mmol) under nitrogen. To this was added 5N NaOH (25 mL) at 0 °C. A solution of p-toluene sulfonyl chloride (14.0 g, 73.43 mmol) in THF (30 mL) was added drop wise to the reaction mixture at 0 °C for 30 min. The resulting mixture was warmed to room temperature and allowed to stir overnight. The mixture was then poured into water (200 mL) and extracted with dichloromethane (2 × 50 mL). The organic extracts were combined and then washed with a brine solution followed by drying with MgSO₄. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel with hexane/ethyl acetate (8:2, v/v) to give the product as colorless needles (6.52 g, 78 %). ¹H NMR (δ/ppm, CDCl₃): 7.81 (d, 2H, Ph-H), 7.37 (d, 2H, Ph-H), 4.36 (dd, 4H, Oxetane-CH₂), 4.12 (s, 2H, O-CH₂), 2.47 (s, 3H, CH₃-C), 1.32 (s, 3H, CH₃-Ph); ¹³C NMR (δ/ppm, CDCl₃): 145.5, 133.0, 130.4, 128.3, 79.3, 74.6, 39.6, 22.0, 21.0. MS. Calcd for: C₁₂H₁₆O₄S (256.08); Found: 257.07 (M+H).

Example (4b) - 3-Methyl-3-((4-(thiophen-3-yl)phenoxy)methyl)oxetane.

[00173] A solution containing 4-(thiophen-3-yl)-phenol (1.0 g, 5.67 mmol), potassium carbonate (2.35 g, 17.02 mmol), and a catalytic amount of benzyl triethylammonium chloride in DMF (50 mL) was stirred under nitrogen for 30 min. The temperature was increased to 60 °C and then stirred for 1h under nitrogen.
Toluene-(4-sulfonic acid 3-methyl-oxetan-3-yl) methyl ester (2.2 g, 8.51 mmol) in anhydrous DMF (50 mL) was added drop wise to the reaction mixture over a period of 30 min. The temperature was maintained at 75 °C for 16 h. The remaining K2CO3 was filtered off and the filtrate was poured into water (200 mL) and then extracted with diethyl ether. The organic layer was washed with water (3 × 100 mL) and dried with MgSO4. The solvent was removed under vacuum and the residue was purified by flash chromatography on silica gel with hexane/ethyl acetate (1:1, v/v) to give the product as a white solids (1.6 g, 98%).

1H NMR (δ/ppm, CDCl3): 7.55 (d, 2H, Ph-H), 7.36-7.40 (m, 3H, Th-H), 6.98 (2H, Ph-H), 4.66 (d, 4H, Oxetane-CH2), 4.49 (d, 4H, Oxetane-CH2), 4.02 (2H, O-CH2), 1.48 (s, 3H, CH3); 13C NMR (δ/ppm, CDCl3): 158.7, 142.3, 129.4, 128.0, 126.5, 126.6, 119.4, 115.2, 80.2, 73.2, 40.1, 21.7. MS. Calcd for: C18H16O2S; 260.09; Found: 261.09 (M+H).

Example (4c) - 3-(4-((3-Methyloxetan-3-yl)methoxy)phenyl)thiophene-2,5-dicarbaldehyde.

[00174] To a solution of 3-methyl-3-((4-(thiophen-3-yl)phenoxy)methyl)oxetane (1.0 g, 3.84 mmol) and freshly distilled TMEDA (2.88 mL, 19.2 mmol) in anhydrous hexanes (30 mL) under nitrogen, was added a solution of 2.5 M n-BuLi in hexane (9 mL, 19.2 mmol) drop wise. After refluxing for 1.5 hours, THF (20 mL) was added and the solution was cooled at -78 °C. Anhydrous DMF (3 mL, 38.7 mmol) was added drop wise. After 2.5 hours at room temperature, the reaction mixture was hydrolyzed with water (100 mL) and
the mixture was extracted with ether. The organic layers were dried over MgSO₄ and concentrated. The crude product was purified by silica column chromatography with hexane/ethyl acetate (3:7, v/v) to give the product as a yellow liquid (0.8 g, 65%). ¹H NMR (δ /ppm, CDCl₃): 10.05 (s, 1H, -CHO), 9.99 (s, 1H, -CHO), 7.84 (s, 1H, Th-H), 7.44 (d, 2H, Ph-H), 7.08 (d, 2H, Ph-H), 4.66 (d, 4H, Oxetane-CH₂), 4.51 (d, 4H, Oxetane-CH₂), 4.12 (s, 2H, O-CH₂), 1.49 (s, 3H, CH₃); ¹³C NMR (δ /ppm, CDCl₃): 185.1, 183.8, 160.4, 150.8, 147.9, 143.4, 137.2, 131.1, 125.9, 115.5, 80.1, 72.2, 62.1, 19.6. MS. Calcd for: C₁₁H₁₆O₄S; 316.08; Found: 317.09 (M+H).

Example (4d) - Tetraethyl-5,5'-((1E,1E)-((3-(4-((3-methyloxetan-3-yl)methoxy)phenyl)thiophene-2,5-diyl)bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate).

In absolute ethanol (60 mL) were dissolved 3-(4-((3-methyloxetan-3-yl)methoxy)phenyl)thiophene-2,5-dicarbaldehyde (100.0 mg, 0.317 mmol) and diethyl 2,5-diaminothiophene-3,4-dicarboxylate (0.82 mg, 0.317 mmol) to which was then added a 1 M solution of TFA (50 μL) followed by stirring for 16 h. The ethanol was evaporated and the product was extracted into dichloromethane followed by washing the organic layer with water (2 x 100 mL). The organic layers were combined and dried over Na₂SO₄ and then concentrated after filtering. The crude product was purified by silica column chromatography with hexane/ethyl acetate (3:7, v/v) to give the product as a red solid (0.14 g, 56%).
$^1$H NMR (δ/ppm, CDCl$_3$): 7.97 (s, 1H, -CH=N-), 7.94 (s, 1H, -CH=N-), 7.04 (s, 1H, Th-H), 6.36 (d, 4H, Th-NH$_2$), 7.08 (d, 2H, Ph-H), 4.66 (d, 4H, Oxetane-CH$_2$), 4.51 (d, 4H, Oxetane-CH$_2$), 4.43 (dd, 8H, CO-CH$_2$), 4.11 (s, 2H, 0-CH$_2$), 1.60 (s, 3H, CH$_3$), 1.34 (t, 6H, C-CH$_3$), 1.28 (t, 6H, C-CH$_3$); $^{13}$C NMR (δ/ppm, CDCl$_3$):

165.7, 163.1, 160.1, 159.9, 158.8, 142.3, 136.3, 135.0, 135.4, 134.2, 127.6, 128.3, 126.2, 122.1, 124.1, 114.7, 82.4, 76.7, 71.2, 61.0, 38.2, 28.4, 19.6, 14.6.

MS. Calcd for: C$_{37}$H$_{40}$N$_2$O$_1$S$_3$; 796.19; Found: 797.19 (M+H).

Example (4e) - 2-(2,5-Dibromo-thiophen-3-yl)-ethanol.

Example (4f) - 3-[2-(2,5-Dibromo-thiophen-3-yl)-ethoxymethyl]-3-methyl-oxetane.
[00177] A solution containing 2-(2,5-dibromo-thiophen-3-yl)-ethanol (2.7 g, 9.44 mmol), potassium hydroxide (2.1 g, 37.76 mmol), and THF (60 mL) was stirred under nitrogen for 30 min. Toluene-(4-sulfonic acid 3-methyl-oxetan-3-yl) methyl ester (3.02 g, 11.81 mmol) dissolved in anhydrous THF (20 mL) was added dropwise over a period of 30 min. The reaction mixture was then refluxed at 75 °C for 16 h. The solution was poured into water (200 mL) and extracted with diethyl ether. The organic layer was washed with water (3 x 100 mL) and dried with MgSO₄. The solvent was removed under vacuum after filtering and the residue was purified by flash chromatography on silica gel with hexanes/ethyl acetate (1:1, v/v) to give the product as a white solid (2.12 g, 61%). ¹H NMR (δ/ppm, CDCl₃): 6.87 (s, 1H, Th-H), 4.48 (d, 2H, Oxetane-CH₂), 4.35 (d, 2H, Oxetane-CH₂), 3.61 (t, 2H, O-CH₂), 3.5 (s, 2H, Oxetane-O-CH₂), 2.81 (t, 2H, Th-CH₂), 1.3 (s, 3H, -CH₃); ¹³C NMR (δ/ppm, CDCl₃): 139.9, 132.8, 111.3, 109.4, 80.8, 76.8, 71.6, 40.2, 30.2, 14.9. MS. Calcd for: C₇₈H₁₉Br₂O₂S; 367.91; Found: 368.89 (M+H).

Example (4g) - 3-(2-((3-Methyloxetan-3-yl)methoxy)ethyl)thiophene-2,5-dicarbaldehyde.
To a solution of 3-[2-(2,5-dibromo-thiophen-3-yl)-ethoxymethyl]-3-methyl-oxetane (1.7 g, 4.64 mmol) in THF (60 mL) was added a solution of 1.6 M n-BuLi in hexanes (10 mL, 16.07 mmol) drop-wise at -78 °C. After 1.5 hours, anhydrous DMF (3 mL, 38.7 mmol) was added drop wise. After 1 hr the dry ice bath was removed and the reaction was continued to stir at room temperature for 16 hr. The reaction mixture was hydrolyzed with water (100 mL) and the mixture was extracted with diethyl ether. The organic layers were dried over MgSO₄ and then concentrated after filtering. The crude product was purified using silica column chromatography with hexanes/ethyl acetate (1:1, v/v) to give the product as a yellow oil (0.76 g, 58 %).

**Example (4h)**

Tetraethyl 5,5′-(((1E,1E)-((3-(2-(3-(3-ethylthiophene-2,5 diyl)bis(methanylylidene))bis(azanylylidene))bis-(2-aminothiophene-3,4-dicarboxylate).
dichloromethane and the organic layer was washed with water (2 x 100 mL). The organic layers were dried over Na₂SO₄ and concentrated after filtering. The crude product was purified by silica column chromatography with hexanes/ethyl acetate (3:7, v/v) to give the product as a red solid (0.56 g, 48%). ¹H NMR (δ/ppm, CDCl₃): 8.0 (s, 1H, -CH=N-), 7.91 (s, 1H, -CH=N-), 7.17 (s, 1H, Th-H), 6.46 (d, 4H, Th-NH₂), 4.46 (dd, 4H, Oxetane-CH₂), 4.33 (dd, 4H, CO-CH₂), 4.23 (dd, 4H, CO-CH₂), 3.68 (s, 2H, O-CH₂), 3.68 (t, 2H, O-CH₂), 3.37 (s, 2H, 0-CH₂), 3.03 (t, 2H, Th-CH₂), 1.45 (t, 6H, COOCH₂CH₃), 1.31 (t, 6H, COOCH₂CH₃), 1.27 (s, 3H, CH₂); ¹³C NMR (δ/ppm, CDCl₃): 163.7, 162.7, 160.2, 159.2, 138.3, 135.9, 134.2, 129.2, 126.1, 121.1, 82.4, 76.7, 71.2, 61.0, 38.2, 28.4, 19.6. 14.6. MS. Calcd for: C₃₇H₄₀N₄O₁₀S₃; 748.19; Found: 749.21 (M+H).

Example (41) - Di-tert-butyl 2,5-diaminothiophene-3,4-dicarboxylate.

In a vial were dissolved tert-butyl cyanoacetate (5 g, 35.4 mmol), elemental sulphur (568 mg, 17.7 mmol) and triethylamine (1.5 mL, 10.63 mmol) in dimethylformamide (3.5 mL). The reaction was stirred at room temperature for 72 hrs. The resulting slurry was then poured into water and filtered to remove the residual sulphur. The filtrate was extracted into ethyl acetate, dried over MgSO₄, filtered, concentrated and then purified by silica gel column chromatography (70/30 hexanes/ethyl acetate). The title compound was isolated as an orange solid (736 mg, 16%). ¹H NMR (400 MHz, acetone-d₆) δ 5.88 (d, J= 9.6Hz, 0.8H), 1.52 (s, 9H).

Example (4j) - Tetra-tert-butyl 5,5'-(1E, 1'E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-aminoth iophene-3,4-dicarboxylate).
In a round bottom flask were dissolved 2,5-thiophenedicarboxylate (50 mg, 0.35 mmol) and di-tert-butyl 2,5-diaminothiophene-3,4-dicarboxylate (280 mg, 0.89 mmol) in anhydrous ethanol (20 mL). A catalytic amount of tetrafluoroacetic acid was then added and the reaction mixture was stirred at room temperature for 18 hrs. The solution was then filtered and the precipitate was washed with cold ethanol and hexanes to give the title compound as a red solid (199 mg, 78%). ¹H NMR (400 MHz, acetone-d₆) δ 8.19 (s, 2H), 7.52 (s, 2H), 7.30 (s, 2.1 H), 1.63 (s, 18H), 1.55(s, 18H) HRMS (ESI) calculated for C₃₄H₄₄N₄O₈S₃ (M+Na)⁺: 755.221 35 found 755.2201.

Example (4k) - Tetraethyl 5,5'-(1E, 1E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-(benzylamino)thiophene-3,4-dicarboxylate).

[00182] The mixture of tetraethyl 5,5'-(1E,rE)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (0.31 g, 0.5 mmol), 2-picoline boron complex (169 mg, 1 mmol) and benzaldehyde (0.106 g, 1 mmol) in a methanol/acetic acid (10:1 5.5 mL) mixture was stirred at room temperature overnight. The reaction was quenched with 1M HCl, neutralized with sodium bicarbonate, extracted with ethyl acetate. The organic phase was dried with sodium sulfate and the solvent removed under reduced pressure. The crude product was purified by silica gel chromatography (hexanes/acetone 3:1) to give the title product as dark red solid (0.12 g, 30%).
Mp 217-218 °C. $^1$H NMR (400 MHz, d-acetone and one drop of D$_2$O) δ 8.20 (s, 2H), 7.48 (s, 2H), 7.45-7.32 (m, 10H), 4.64 (s, 4H), 4.36 (q, J = 7.1 Hz, 4H), 4.21 (q, J = 7.1 Hz, 4H), 1.41 (t, J = 7.1 Hz, 6H), 1.27 (t, J = 7.1 Hz, 6H). HRMS: Calcd for C$_{40}$H$_{40}$N$_{40}$S$_3$ (M+H)$^+$: 801.2081, found: 801.2080.

5 Example (41) - Tetraethyl 5,5'-(1E,1'E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-(decylamino)thiophene-3,4-dicarboxylate).

![Chemical structure](image)

[00183] The mixture of 5,5'-(1E,1'E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (0.31 g, 0.5 mmol), 2-picoline boron complex (169 mg, 1 mmol) and decanal (0.156 g, 1 mmol) in a mixture of methanol/acetic acid (10:1 5.5 mL) was stirred at room temperature overnight. The reaction was then quenched with 1M HCl, neutralized with sodium bicarbonate, and then extracted with ethyl acetate. The organic layer was dried with sodium sulfate, filtered and the crude product purified by silica gel chromatography to give the title product as dark red solid (0.095 g, 21%). Mp 60-62 °C. $^1$H NMR (400 MHz, d-acetone and D$_2$O) δ 8.220 (s, 2H), 7.478 (s, 2H), 4.37 (q, J = 7.2 Hz, 4H), 4.20 (q, J = 7.2 Hz, 4H), 3.37 (t, J = 7.0 Hz, 4H), 1.74 (m, 4H), 1.43 (m, 12H), 1.34 (m, 28H), 0.87 (t, J = 7.2 Hz, 6H). $^{13}$C NMR (100 MHz, d-acetone and D$_2$O) 6165.052, 164.653, 163.019, 146.128, 144.668, 132.615, 132.388, 132.137, 100.261, 61.250, 60.177, 47.926, 32.124, 27.014, 22.830, 14.391, 14.075, 13.888. HR-MS (ESI) Calcd for C$_{40}$H$_{40}$N$_{40}$S$_3$ (M+H)$^+$: 901.4272, found: 901.4274.
Example (4m) - Tetraethyl 5,5'-((1E, 1E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-((4-(tert-butyl)amino)thiophene-3,4-dicarboxylate).

In a round bottom flask was added tetraethyl 5,5'-((1E,1'E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (332 mg, 0.535 mmol), ferf-butyl 4-formylbenzoate (150 mg, 1.07 mmol), and picoline borane (14 mg, 1.07 mmol) and dissolved in a 1:10 mixture of acetic acid/methanol (5 mL). The mixture was stirred at room temperature overnight and then quenched with water. The aqueous layer was neutralized with sodium carbonate and the crude product was extracted into ethyl acetate. The organic layer was dried over magnesium sulfate, filtered, and the solvent removed to give the title product.

Example (4n) - 4,4'-(5,5'-(1E,1'E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(3,4-bis(ethoxycarbonyl)thiophene-5,2-diyl)bis(azanediyl) dibenzoic acid.
Tetraethyl 5,5'-(1E,1E)-(thiophene-2,5-diylbis(methanylylidene))bis(azanylylidene))bis(2-((4-(tert-butoxycarbonyl)
phenyl)amino)thiophene-3,4-dicarboxylate) was dissolved in dichloromethane to which was then added trifluoroacetic acid (2 mL). The mixture was stirred at room

temperature overnight and the pure product was filtered from the solution.

Example 5 - Electrolyte gel preparation

The standard electrolyte gel used was prepared from an acetonitrile solution of poly(methylmethacrylate) (M_n=110,000 g/mol), propylene carbonate (PC) in weight ratios of 1:0.1:0.4. To this solution, was added tetrabutylammonium hexafluoro phosphate (optimized, 0.5 M concentration relative to acetonitrile). The solution was heated at 50 ºC for 10 min. for complete dissolution of the reagents. However, other suitable electrolytic gels known to those skilled in the art can also be used.

Example 6 - Electrochromic device fabrication

Example (6a)

5,5'-(1E,1E)-((3-(2-((3-methyloxetan-3-yl)methoxy)ethyl)thiophene-2,5-diyl)bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene-3,4-dicarboxylate) (from Example 4h) was dissolved in dichloromethane and spin coated onto an ITO covered glass substrate at 3000 rpm for 40 sec. The electrochromic layer was then immobilized by exposing it to a saturated atmosphere of BF_3:Et_2O for 18 hrs. The substrate was then washed with a 10 weight % triethylamine in dichloromethane. The thickness of the cross-linked electrochromic layer was between 70 and 80 nm.

Example (6b)

Alternatively, 5,5'-(1E,1'E)-((3-(2-((3-methyloxetan-3-yl)methoxy)ethyl)thiophene-2,5
diyl)bis(methanylylidene))bis(azanylylidene))bis(2-aminothiophene dicarboxylate) (from Example 4h) was dissolved in dichloromethane with 5 weight % bis-(4-fert-butyl-phenyl)-iodonium hexafluoroantimonate and the photoacid generator followed by spin coating onto an ITO covered glass substrate at 3000 rpm for 40 sec. The substrate was irradiated with visible light for 60 min. after which the substrate was washed with a 10 weight % triethylamine in dichloromethane. The thickness of the cross-linked electrochromic layer was between 70 and 80 nm.

[00189] On a separate ITO covered glass substrate was spin coated the electrolytic gel at 3000 rpm for 40 sec.

[00190] The two glass substrates were assembled with the following architecture: glass-ITO/electrolytic gel/electrochromic layer/ITO-glass. The fabricated electrochromic device was then heated at 40 °C under reduced pressure for 5-10 min to evaporate excess acetonitrile resulting in a working electrochromic device. Colors changes resulted when applying potentials between 1 and 2 V vs. Ag/Ag⁺. The original color resulted when applying a potential between 0 and -500 mV vs. Ag/Ag⁺.

*Example 7* On-Substrate Electrochromic Device Fabrication

*Film Preparation*

[00191] The films are prepared by spray coating the monomers onto 1.5 x 2 cm conductive glass substrates. A mixture of the two monomers in a 1:1 stoichiometry was prepared in 1 mL of dichloromethane (DCM). This mixture was loaded in to a spray gun connected to an air compressor. The mixture was then spread evenly with the spray gun on the slides from a distance of 10 cm using circular motions. The thickness of the resulting films can be adjusted between 50 and 500 nm by varying the concentration of the monomer solution

*Polymerization*
The slides are placed on a hot plate along with a small vial containing 1 mL of trifluoroacetic acid (TFA). A glass dish was then set on top in order to create a small chamber around the samples. The heating was adjusted between 60 and 150°C. Once a TFA saturated atmosphere was achieved, the slides were polymerized for between 15 and 45 minutes. After cooling, the slides were washed with triethylamine that was diluted in DCM followed by pure DCM.

**Gel electrolyte preparation**

The gel electrolyte was prepared by adding together propylene carbonate (PC), poly(ethylene glycol) diacrylate (PEG-DA), and tetrabutylammonium tetrafluoroborate (TBA-TFB) in the respectively weight ratio of 20:14:6. 2,2-Dimethoxy-2-phenylacetophenone was used as the photoinitiator, which was added to the gel mixture with a proportion of 17.5 mg for 5 g of PC.

**Device fabrication**

A frame of double-sided adhesive foam tape was placed on a blank 1.5 x 2 cm ITO-coated glass slide, leaving a half a centimeter bare on one side. The gel electrolyte was deposited inside the frame with a Pasteur pipette. The polymer film coated ITO-glass slide was then placed on top of the gel coated ITO-glass. The device was then placed in a UV chamber for five minutes to cure the gel. The gel was cross-linked and sealed by irradiating it with three 380 nm lamps for between 5 and 10 minutes. Copper tape was finally applied to both slides to serve as electrical contacts.

**Example 8 - Immobilization of 4(d) and 4(h) on a Substrate**

A 10 mg/mL solution of either oxetane derivative 4D or 4H was prepared by dissolving it in THF. A photoacid generator, photosensitizer, and a cationic accelerator were added to the oxetane in 0.5/0.25/0.4 wt %. The photoacid generator used was [4-[(octyloxy)phenyl] phenyl] iodonium hexafluoroantimonate. Any photoinitiator can be used. The photoinitiator used was HU-470. Any photosensitizer, such as xanthate or fluorene derivatives,
having an absorbance different than 4D or 4H and known to those skilled in the art, can also be used. The cationic accelerator was AN-910-E. The resulting solution was mixed while protecting it from ambient light. It was then deposited onto conductive substrates as per paragraph 122. A pattern was placed on top of the substrate and it was irradiated with a 350 nm lamp for 2 minutes. The substrate was then backed at 100°C for 60 minutes, after which it was rinsed with either THF or dichloromethane and then air dried. The electrochromic device was completed and it could repeatedly be switched between its neutral and oxidized states by applying forward and reverse potentials of up to +3 and -3 V, respectively.
### Table 1: Photophysical and Electrochemical Properties of Various Fluorenylazomethimes

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ_{abs} (nm)</th>
<th>λ_{θ} (nm)</th>
<th>λ_{abs} with added TFA (nm)</th>
<th>λ_{abs} with added FeCl₃ (nm)</th>
<th>E_{\text{g},\text{opt}} (eV)</th>
<th>E_{\text{pe}} (V)</th>
<th>E_{\text{pc}} (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>E_{\text{g}}^\text{st} (eV)</th>
<th>Φ_B (H+)</th>
<th>Φ_B 77 K</th>
<th>Φ*</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFI-co-DAT</td>
<td>514, 553 (516,558)</td>
<td>576 (622)</td>
<td>565</td>
<td>600/652</td>
<td>2.11</td>
<td>0.93</td>
<td>-0.98</td>
<td>5.16</td>
<td>3.47</td>
<td>1.7</td>
<td>0.13 (0.66)</td>
<td>3x</td>
<td>0.11</td>
</tr>
<tr>
<td>PFI-co-Th</td>
<td>415 (438)</td>
<td>473 (546)</td>
<td>475</td>
<td>440/595</td>
<td>1.58</td>
<td>0.84</td>
<td>-1.05</td>
<td>4.88</td>
<td>3.67</td>
<td>1.2</td>
<td>0.15</td>
<td>4x</td>
<td>0.09</td>
</tr>
<tr>
<td>PFI-co-EDOT</td>
<td>475 (493)</td>
<td>495 (565)</td>
<td>505</td>
<td>540</td>
<td>2.04</td>
<td>0.71</td>
<td>-1.11</td>
<td>4.98</td>
<td>3.63</td>
<td>1.3</td>
<td>0.26 (0.85)</td>
<td>3x</td>
<td>0.03</td>
</tr>
<tr>
<td>PFI-co-Fl</td>
<td>425 (452)</td>
<td>551 (563)</td>
<td>510</td>
<td>531</td>
<td>2.20</td>
<td>1.54</td>
<td>-0.87</td>
<td>5.94</td>
<td>3.53</td>
<td>2.4</td>
<td>0.19 (0.75)</td>
<td>= 5x</td>
<td>0.4</td>
</tr>
<tr>
<td>Th-Fl-Th₁</td>
<td>388</td>
<td>468</td>
<td>440</td>
<td>450</td>
<td>2.53</td>
<td>0.92</td>
<td>-</td>
<td>5.2</td>
<td>2.67</td>
<td>2.5</td>
<td>0.27 (0.86)</td>
<td>3x</td>
<td>-</td>
</tr>
<tr>
<td>Th-Fl-Th₂</td>
<td>395</td>
<td>475</td>
<td>460</td>
<td>475</td>
<td>2.41</td>
<td>0.90</td>
<td>-</td>
<td>5.16</td>
<td>2.7</td>
<td>2.4</td>
<td>0.12 (0.42)</td>
<td>2x</td>
<td>-</td>
</tr>
</tbody>
</table>

*Spin coated Samples-Thin film. Units: fl.

---

a In dichloromethane. Values in parentheses are for thin film samples. b Spectroscopically determined energy gap taken from the absorption onset (E_g=1240/λ_{\text{max}}). c Oxidation potential relative to saturated Ag/Ag⁺ electrode. d Reduction potential relative to Ag/Ag⁺. e Relative to the vacuum level. f Electrochemically derived energy gap. g Absolute fluorescence quantum yield at room temperature. Values in parentheses are the room temperature absolute fluorescence quantum yield upon protonation with TFA. h Fluorescence enhancement at 77 K relative to room temperature and uncorrected for the change in refractive index at different temperatures. i Spin coated samples. j From reference.
Table 2. Molecular weights and thermal properties of various polyazomethines.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$ (g/mol)$^a$</th>
<th>$M_n$ (g/mol)$^b$</th>
<th>$M_w$ (g/mol)$^b$</th>
<th>PDI$^b$</th>
<th>DP,</th>
<th>$T_d$ (°C)$^c$</th>
<th>$T_g$ (°C)$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PFI-co-Th</td>
<td>7 176</td>
<td>7 747</td>
<td>9 330</td>
<td>1.20</td>
<td>13</td>
<td>330</td>
<td>115</td>
</tr>
<tr>
<td>PFI-co-DAT</td>
<td>15 092</td>
<td>16 407</td>
<td>22 151</td>
<td>1.35</td>
<td>23</td>
<td>320</td>
<td>146</td>
</tr>
<tr>
<td>PFI-co-EDOT</td>
<td>6 648</td>
<td>6 858</td>
<td>11 815</td>
<td>1.72</td>
<td>13</td>
<td>380</td>
<td>148</td>
</tr>
</tbody>
</table>

$^a$Determined by $^1$H-NMR. $^b$Determined by GPC relative to polystyrene standards. $^c$Determined by thermal analysis measured at 10 °C/min under $N_2$. $^d$Determined by DSC measured at a 5 °C/min under $N_2$. 
CITATIONS FOR REFERENCES REFERRED TO IN THE SPECIFICATION

CLAIMS:

1. A polymer of the formula I

$$\begin{align*}
\text{H}_2\text{N} & \left( \begin{array}{c} 
\text{R}_1 \\
\text{R}_2 \\
\text{R}_3 \\
\text{R}_4
\end{array} \right)
\end{align*}$$

wherein,

5. $\text{R}_1$ is alkylene, cycloalkylene, alkenylene, alkynylene, arylene, heteroarylene, NH-alkyl, NH-aryl, N(alkyl)alkyl, N(alkyl)-aryl, or $n \text{R}_4 \text{C}(0) - \text{R}_5 \cdot \text{C}(0) \text{NR}_4$;

$\text{R}_2$ is alkylene, arylene or heteroarylene;

$\text{R}_3$ is hydrogen, alkyl, aryl or heteroaryl;

$\text{R}_4$ is alkyl, aryl or heteroaryl;

10. $\text{R}_5$ is alkylene, arylene or heteroarylene; and

$n$ is an integer from 2 to 100,

wherein the alkyl(ene), cycloalkyl(ene), alkenyl(ene), alkynyl(ene), aryl(ene) or heteroaryl(ene) groups are each optionally substituted with one to five substituents independently selected from halo, hydroxy, CN, C(0)NH2, C1-14-alkyl, C3-Cio-cycloalkyl, C(0)-aryl and -C(0)OR, or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, wherein $\text{R}$ is H, C1-C6-alkyl (such as t-butyl) or aryl.

2. The polymer according to claim 1, wherein

$\text{R}_1$ is C1-C10-alkylene, C3-Cio-cycloalkylene, C2-C6-alkenylene, C2-C10-alkynylene, C6-C14-arylene, or C5-C14-heteroarylene;

$\text{R}_2$ is CrCio -alkylene, C6-C14-arylene or C5-C14-heteroarylene; and

$\text{R}_3$ is hydrogen, C1-Cio -alkyl, C6-C14-aryl or C5-C14-heteroarylene.

3. The polymer according to claim 1 or 2, wherein
\( R_1 \) is \( \text{Ci-C6-alkylene, C6-Ci-arylene, or C5-Ci4-heteroarylene.} \)

4. The polymer according to claim 3, wherein \( R_1 \) is selected from thiophenylene, phenylene, fluorene, and hexylene.

5. The polymer according to claim 4, wherein \( R_1 \) is selected from

\[
\begin{align*}
\text{EtO}_2\text{C} & \quad \text{CO}_2\text{Et}, \\
\text{C}_6\text{C}_{13} \quad \text{C}_6\text{C}_{13} & \quad \text{and}
\end{align*}
\]

6. The polymer according to any one of claims 1 to 5, wherein \( R_2 \) is selected from thiophenylene, phenylene and fluorene.

7. The polymer according to claim 6, wherein \( R_2 \) is selected from
8. The polymer according to any one of claims 1 to 7, wherein $R_3$ is hydrogen.

9. The polymer according to any one of claims 1 to 8, wherein the compound of the formula I is

![Chemical Structure]

10.
wherein \( n \) is an integer from 2 to 100.

10. A polymer of the formula (II)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \left( \text{H}_2\text{C}_6 \right) \quad \text{N} \quad \text{O} \\
\text{H}_2\text{N} & \quad \left( \text{H}_2\text{C}_6 \right) \quad \text{N} \quad \text{O} \\
\end{align*}
\]

wherein

\( R_6 \) is as defined for \( R_1 \) in any one of claims 1 to 9,
\( R_7 \) is as defined for \( R_3 \) in any one of claims 1 to 9; and
\( p \) is an integer from 2 to 100.

11. A polymer of the formula (I) according to claim 1, which is a compound of the formula (Ia)

\[
\begin{align*}
\text{H}_2\text{N} & \quad \left( \text{R}_{1a} \right) \quad \text{N} \quad \text{O} \\
\end{align*}
\]

wherein,

\( R_{1a} \) is arylene or heteroarylene;
\( R_{2a} \) is arylene or heteroarylene;
\( R_{3a} \) is hydrogen or alkyl; and

\( r \) is an integer from 2 to 100;

wherein the alkyl(ene), cycloalkyl(ene), alkenyl(ene), alkynyl(ene), aryl(ene) or heteroaryl(ene) groups are each optionally substituted with one to five substituents independently selected from halo, hydroxy, CN, \( C(0)NH_2 \), \( C1-14 \)-alkyl, \( C_3-Ci_0 \)-cycloalkyl, \( C(0) \)-aryl and \( C(0)OR \), or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, wherein \( R \) is \( H, C1-C6-alkyl \) (such as t-butyl) or aryl.

12. The polymer according to claim 11, wherein one of \( R_{1a} \) or \( R_{2a} \) is a 9,9-di-substituted fluorene moiety of the formula (A)

\[
\begin{array}{c}
\text{R'} \\
\text{R'}
\end{array}
\]

wherein \( R' \) are each independently or simultaneously \( C1-14 \)-alkyl or \( C3-C10 \)-cycloalkyl, wherein the benzene rings of the fluorene monomer are optionally substituted with the substituents with one to three substituents selected from halo, hydroxy, \( C1-14 \)-alkyl, \( C3-Ci_0 \)-cycloalkyl and \( C(0)OR \), or two adjacent hydroxy substituents are joined together with the atoms to which they are attached to form a 5- or 6-membered ring, and wherein \( R \) is \( C1-C6-alkyl \).

13. The polymer according to claim 11 or 12, wherein \( R_{1a} \) is fluorene or thiophenylene.
14. The polymer according to claim 13, wherein $R_{1a}$ is

15. The polymer according to claim 11 or 12, $R_{2a}$ is fluorene or thiophenylene.

16. The polymer according to claim 15, wherein $R_{2a}$ is

17. The polymer according to any one of claims 11 to 16, wherein $R_{3a}$ is hydrogen.
18. The polymer according to any one of claims 11 to 17, wherein the compound of the formula (la) is

\[
\begin{array}{c}
\text{PFI-co-Th} \\
\end{array}
\]

or

\[
\begin{array}{c}
PFI\text{-co-DAT} \\
\end{array}
\]

or

\[
\begin{array}{c}
PFI\text{-co-EDOT} \\
\end{array}
\]

19. A method for the dynamic polymerization of a polymer of formula (I), (la) or (II) as defined in any one of claims 1 to 18, comprising:

(i) contacting the polymer of formula (I), (la) or (II) with a compound of the formula (III), (IV) or (V):

(a) formula (III)

\[
\begin{array}{c}
\text{R}_g \\
\end{array}
\]

wherein,

\( \text{R}_g \) is as defined for \( \text{R}_3 \) in any one of claims 1 to 9;

\( \text{R}_g \) is as defined for \( \text{R}_3 \) in any one of claims 1 to 9; and

(b) formula (IV)
(IV)

wherein,

\( R_{10} \) is as defined for \( R_1 \) in any one of claims 1 to 9;

c) formula (V)

(V)

wherein,

\( R_{11} \) is as defined for \( R_1 \) in any one of claims 1 to 9;

\( R_{12} \) is as defined for \( R_3 \) in any one of claims 1 to 9; and

(ii) heating the polymer of the formula (I), (Ia) or (II) with the compound of

the formula (III), (IV) or (V) to a temperature, and for a time, for dynamic polymerization to occur.

20. The method according to claim 19, wherein the temperature for dynamic polymerization is between 50° and 200°C.

21. The method according to claim 19, wherein the time for dynamic polymerization is between 2 minutes and 120 minutes.

22. The method according to any one of claims 19 to 21, wherein the method is conducted in the presence of a catalyst.

23. The method according to claim 22, wherein the catalyst is an organic acid such as trifluoroacetic acid, methane sulfonic acid or triflic acid; a mineral acid such as sulfuric acid, hydrochloric acid or nitric acid; or a Lewis acid such as boron trifluoride etherate.
24. An azomethine compound of the Formula (VI)

![Structure of formula (VI)](image_url)

wherein:

(a) \( \text{Ri3} \) is selected from the group consisting of CN, C(0)aryl, C(0)NH2 and C02R16;

(b) \( \text{R14} \) is selected from the group consisting of alkyene, orfr/o-arylene, meta-arylene, para-arylene, 1-alkylarylene, alkyene ether, and arylene ether;

(c) \( \text{Ri5} \) is selected from the group consisting of H, alkyl, aryl, =CH and =C-alkyl, with the proviso that when \( \text{R15} \) is =CH or =C-alkyl, the moiety -NH-R15 is -N=RG;

(d) \( \text{Ri6} \) is selected from the group consisting of S, S02, 0, NH, N-alkyl, N-aryl, N-S02H, N-S02-alkyl and N-S02-aryl;

(e) \( \text{R17} \) is selected from the group consisting of alkyl, O-alkyl, O-aryl, aryl, S-alkyl, S-aryl, N02, CN, and C02R11; and

(f) \( \text{R18} \) is selected from the group consisting of H, alkyl, and monovalent organic or inorganic cations.

25. An azomethine compound of the Formula (VII):
wherein:

(a) \( R_{19} \) is selected from the group consisting of CN, C(0)aryl, C(0)NH_2 and CO2R22;

(b) \( R_{20} \) is an arylene or heteroarylene;

(c) \( R_{21} \) is selected from the group consisting of H, alkyl, aryl, =CH-alkyl, =CH-aryl, \( =C \)-alkyl, \( 1,4\)-benzyl-C0 \( 2\)-tert-butyl, \( 1,3\)-benzyl-C0 \( 2\)-tert-butyl, \( 1,2\)-benzyl-C0 \( 2\)-tert-butyl, \( =CH\)-para-phenyl-C0 \( 2\)-tert-butyl, \( =CH\)-ortho-phenyl-C0 \( 2\)-tert-butyl, and \( =CH\)-meta-phenyl-C0 \( 2\)-tert-butyl, with the proviso that when \( R_{21} \) is \( =CH\)-alkyl, \( =CH\)-aryl or \( =C\)-alkyl, the moiety -NH-\( R_{21} \) is -N=\( R_{21} \); and

(d) \( R_{22} \) is selected from the group consisting of H, alkyl, tert-butyl and monovalent organic or inorganic cations.

26. A azomethine polymer of the Formula (VIII):

wherein:

(a) \( R_{23} \) is selected from the group consisting of CN, C(0)NH_2, C(0)-aryl and CO2R25;
(b) \( R_{24} \) is arylene or heteroarylene;

(c) \( R_{25} \) is selected from the group consisting of tert-butyl, \( H \), alkyl and aryl;

and

(d) \( m \) is from 2 to 50.
FIG. 1
FIG. 3
FIG. 6
FIG. 7
FIG. 8
FIG. 11
FIG. 12
FIG. 13
FIG. 16
FIG. 17
FIG. 18
FIG. 19
FIG. 20
INTERNATIONAL SEARCH REPORT

International application No. PCT/CA20 12/000777

A. CLASSIFICATION OF SUBJECT MATTER

IPC: C08G 73/00 (2006.01) . C07D 333/26 (2006.01) . C07D 409/14 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
PC: C08G 73/00 (2006.01 ) , C07D 333/26 (2006.01) , C07D 409/14 (2006.01 )

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
Canadian Patent Database, USPTO, CAPlus, Total Patent, Google [ azomethine, acylhydrazone, fluorescent, electrochOmic]

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US5453515, 26 September 1995 (26-09-1995) abstract, columns 1-4</td>
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[X] See patent family annex.

Further documents are listed in the continuation of Box C.

Date of the actual completion of the international search 30 October 2012 (30-10-2012)

Date of mailing of the international search report 09 November 2012 (09-11-2012)

Authorized officer Reese A. Acleney (819) 997-2852

Canadian Intellectual Property Office
Place du Portage 1, C114 - 1st Floor, Box PCT
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